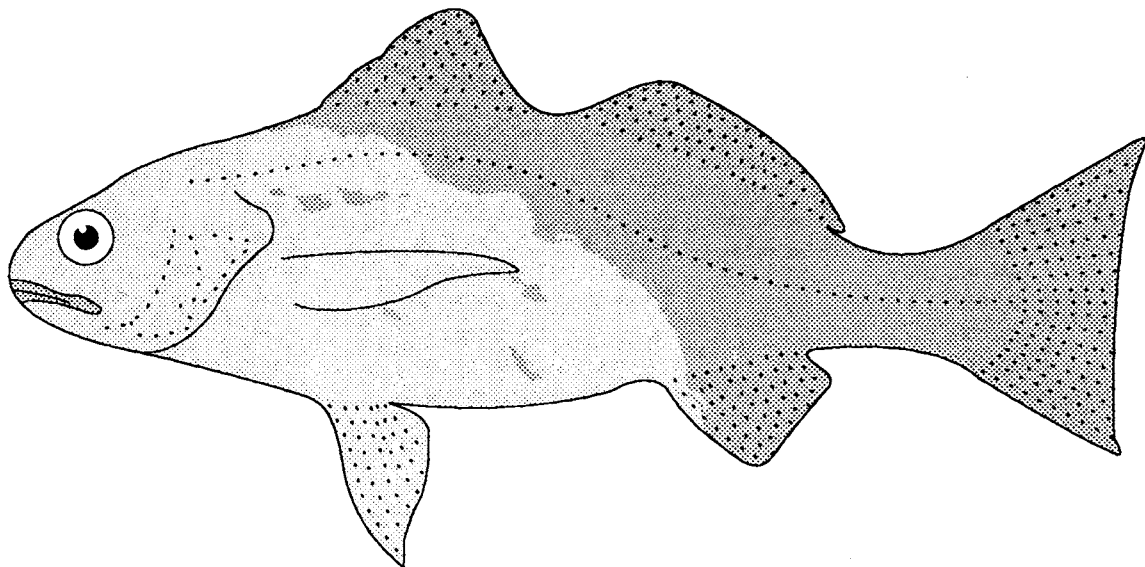NOAA Technical Memorandum NOS ORCA 62

CONTAMINANT TRENDS IN THE SOUTHERN CALIFORNIA
BIGHT: INVENTORY AND ASSESSMENT

Seattle, Washington
October 1991

noaa NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

National Ocean Service

Office of Ocean Resources Conservation and Assessment
National Ocean Service
National Oceanic and Atmospheric Administration
U.S. Department of Commerce

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CONTAMINANT TRENDS IN THE SOUTHERN CALIFORNIA BIGHT: INVENTORY AND ASSESSMENT

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ABSTRACT

This is one of a series of regional reports summarizing existing information on contaminants measured by the National Status and Trends (NS&T) Program. It describes the data that exists for documenting the geographic distribution and long-term trends of 17 groups of contaminants in sediments, mussels, fish, and other species of the Southern California Bight, but not birds and mammals. The report is a companion to a National Research Council (NRC) (1990) report on monitoring in the Southern California Bight. It also provides a guide to contaminant monitoring data sets covering samples collected over the past 50 years. Ten trace elements, organotin compounds, PAHs, PCBs, and several pesticides are reviewed here.

The objectives of this report were to:

1. Determine where in the Southern California Bight sediments, mussels, and fish are contaminated and where they are not.

2. Determine whether levels of contaminants in sediments, mussels, or fish have changed since they were first monitored.

3. Evaluate existing information about contaminants in the Southern California Bight to highlight those contaminants that are of concern. Additionally, some recommendations for monitoring and supporting research are provided.

Although over $18 million has been spent annually on monitoring contaminant concentrations in the Southern California Bight since 1970, the resulting data has remained scattered in reports that are difficult to obtain. There are many inconsistencies in the monitoring data that make comparing sites difficult and analysis of long-term trends impossible in many cases. However, there have been a few surveys that have sampled many sites over long periods with consistent protocols and methods, and these have been used to generate some conclusions regarding contamination in the Southern California Bight.

With the exception of the Palos Verdes Peninsula, the most contaminated sites for sediment, mussels, and fish have occurred in bays and harbors. Highest levels of DDT, PCBs, copper, lead, mercury, or zinc have been found in sediments from Newport Bay, San Diego Harbor, Santa Monica Bay, Marina Del Rey, Los Angeles-Long Beach harbors, and of course, Palos Verdes. The least contaminated areas for sediments are the coastal shelf areas near Santa Barbara, and between southern Orange County and Point Loma. Only some contaminants (chromium, DDT and PCBs) show the same pattern in mussels as in nearby sediments. Highest levels of these contaminants were found at Palos Verdes and Los Angeles-Long Beach harbors. Mussels from Oceanside Harbor, Marina del Rey, San Diego Harbor, and Newport Bay also contained elevated levels of contaminants, but in different patterns than those in sediment. In fish, only the organic contaminants show a similar pattern to that in sediments or mussels. For most metals, highest levels were found in fish from areas remote from known sources, such as Dana Point.

With one interesting exception, the long-term trend data reviewed for this report indicate that no contaminants are increasing in concentration in sediments, mussels, or fish in the Bight. Taken in total, data reviewed for this report suggest that where they were once high, concentrations of most contaminants have been decreasing in sediments and tissues of marine organisms. However, there are many major gaps in the trend monitoring data, most notably for bays, harbors, and lagoons where monitoring has been non-existent. The one exception to the broad pattern of decreasing contamination with time is for cadmium in mussels from Royal Palms on the Palos Verdes Peninsula. Concentrations there have increased during the past 5 years despite reductions in emissions from a nearby sewage outfall.

Criteria imposed to determine which contaminants are of continuing concerns in the Southern California Bight were:

1. Accumulations to excess or potentially toxic levels in sediment.

2. Accumulation in mussels.

3. Accumulation in fish or other species.

4. Biomagnification.

5. Long-term trend of increasing concentrations in sediment, mussels, or other species.

There was evidence that all contaminants have accumulated in sediment, particularly in bays and harbors. However, not all have accumulated to potentially toxic levels. Also, not all contaminants have accumulated in mussels and other species. Only three contaminants showed evidence of biomagnification. Finally, only one compound is apparently increasing in concentration. The chemicals of concern in the Southern California Bight that can be managed by further controlling inputs are DDT, PCBs, chlordane, lead, and PAHs. Mercury and arsenic are naturally high in some species and, while of possible public health concern, cannot be managed through control of regional sources. Those of uncertain concern include tin, cadmium, and silver. Contaminants that are apparently not of concern include chromium, copper, zinc, and dieldrin.

Recommendations for future monitoring and research in the Southern California Bight include better coordination of existing monitoring programs and improved availability of historical data. New sediment cores should be taken to document changes in sediment contamination. Species should be considered for future monitoring that have been sampled in the past, such as kelp bass, Dover sole, scallops, prawns, crabs, and lobster. Lipid content of biological samples should be included with contaminant data. Bays, harbors, and lagoons need further emphasis in regional monitoring programs. Some chemical methods should be improved. Analyses of lead should occur in lead-free laboratory environments, and detection limits for contaminants in waste water should be lowered so that further improvements in waste water treatment can be documented. Since very low levels of DDT, chlordane, and dieldrin in sediment are thought to cause toxic effects in sensitive species, detection limits could be lowered to allow assessment of potential toxicity.

ACKNOWLEDGMENTS

CHAPTER 1

INTRODUCTION

In 1984 NOAA initiated the National Status and Trends (NS&T) Program to monitor marine pollution along the U.S. coastline. The principal goal of the program is to determine trends of contaminant levels in sediments, mussels, oysters, and fish. To help assess contaminant trends and resolve the extent of contamination in major urban areas, the NS&T Program has expanded to include analysis of existing data from other programs, including those conducted by state and local agencies, universities, and private companies. Historical assessment reports have been completed for San Francisco Bay (Long *et al.* 1988), Oregon (Buchman, 1989), Long Island Sound (Turgeon *et al.*, 1989), Boston Harbor (MacDonald, 1991) and Tampa Bay (Long *et al.*, 1991).

This report continues the series by reviewing information on trends of chemical contaminants in sediments, shellfish, and fish of the Southern California Bight (Figures 1.1, 1.2, and 1.3). The major objectives of this report were to:

1. Place recent measures of contaminants, including those from the NS&T Program, into a regionwide perspective with emphasis on determining where sediments, mussels and fish are contaminated and where they are not.

2. Determine long-term trends of commonly monitored chemical contaminants in sediments, mussels, other shellfish, and fish of the Bight.

3. Identify contaminants of most and least concern.

The Bight is of special interest to NOAA because over 10 percent of the national monitoring effort occurs in this densely populated and industrialized coastal zone. Since the NS&T Program began in 1984, components of it, the Benthic Surveillance Project and the Mussel Watch Project have surveyed 20 stations in the Bight. There are several reasons for conducting a review of contaminant trends in this region. First, unlike the situation in many other coastal areas, there is a large body of data available with which to evaluate contaminant trends on local and regional scales. These data are needed to help NOAA determine where marine resources are most at risk from contaminants. Second, despite rapid population growth and intense commercial activity, industries and municipalities along the coast have made major efforts to identify and reduce sources of coastal pollution and monitor the responses during the past 20 years. These efforts should result in declining contamination of marine resources under NOAA's management responsibility, including sediments, fish, shellfish, and marine mammals. Third, NOAA and other agencies have conducted much research and development activities to understand which contaminants are of most concern in an urban coastal setting. It is possible that the available data can now be used to judge contaminants of most and least concern.

It is well known that dichlorodiphenyltrichloroethane (DDT) has been one of the principal contaminants of the Southern California Bight and its living marine resources (Young, Gossett, and Heesen, 1988). To some extent, concern about DDT may have diverted attention from other noteworthy contaminants including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), chlordane, dieldrin, arsenic (As), mercury (Hg), silver (Ag), and lead (Pb). It was decided, therefore, that a more balanced assessment of a wide diversity of contaminants should be conducted, with equal emphasis on each of a large suites of contaminants, and that the data should be evaluated considering an objective framework for evaluating each contaminant.

Figure 1.1. The Southern California Bight in perspective.
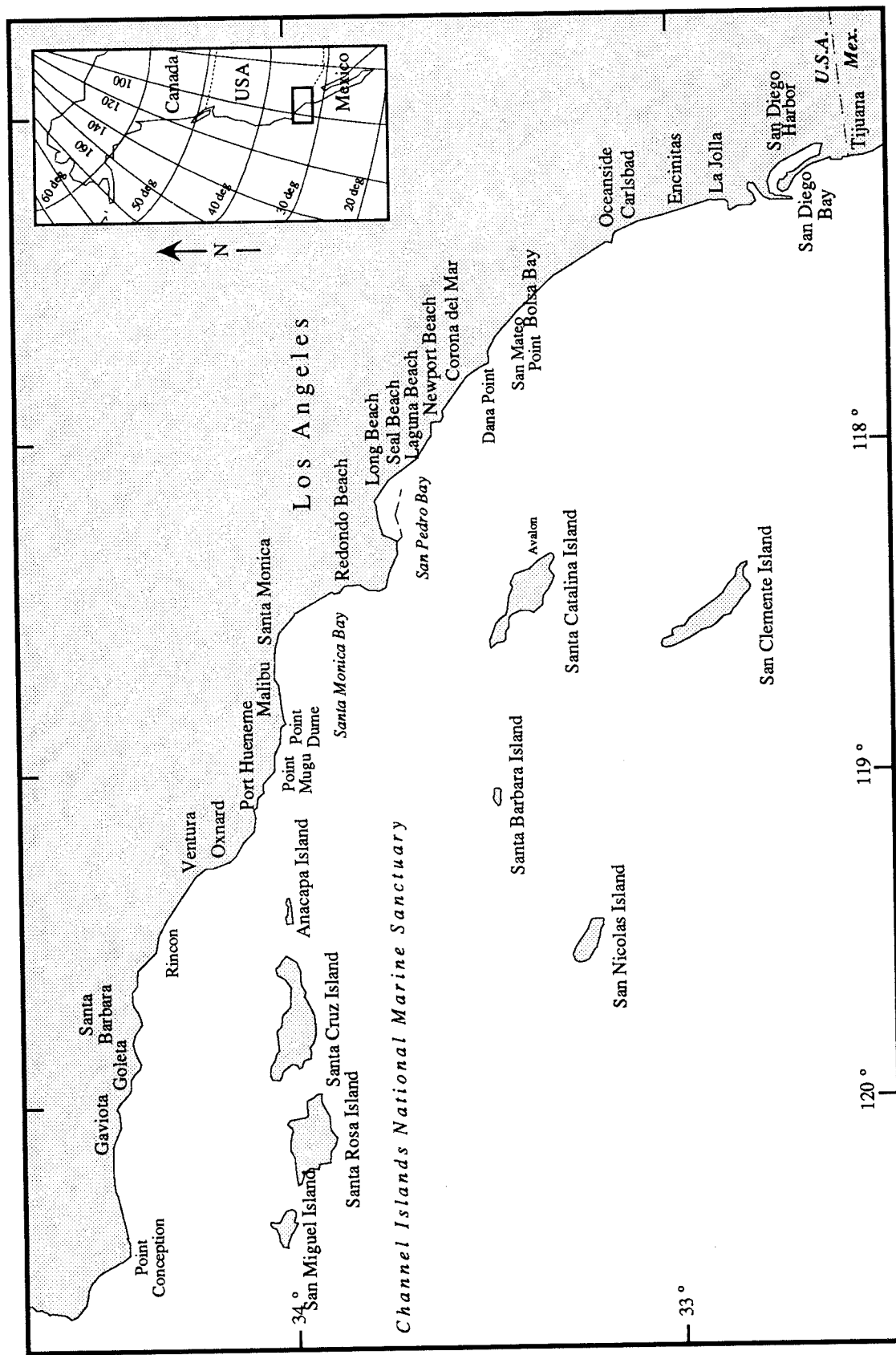
Figure 1.2. General map of the northern portion of the Southern California Bight showing major political features and cities cited in report.
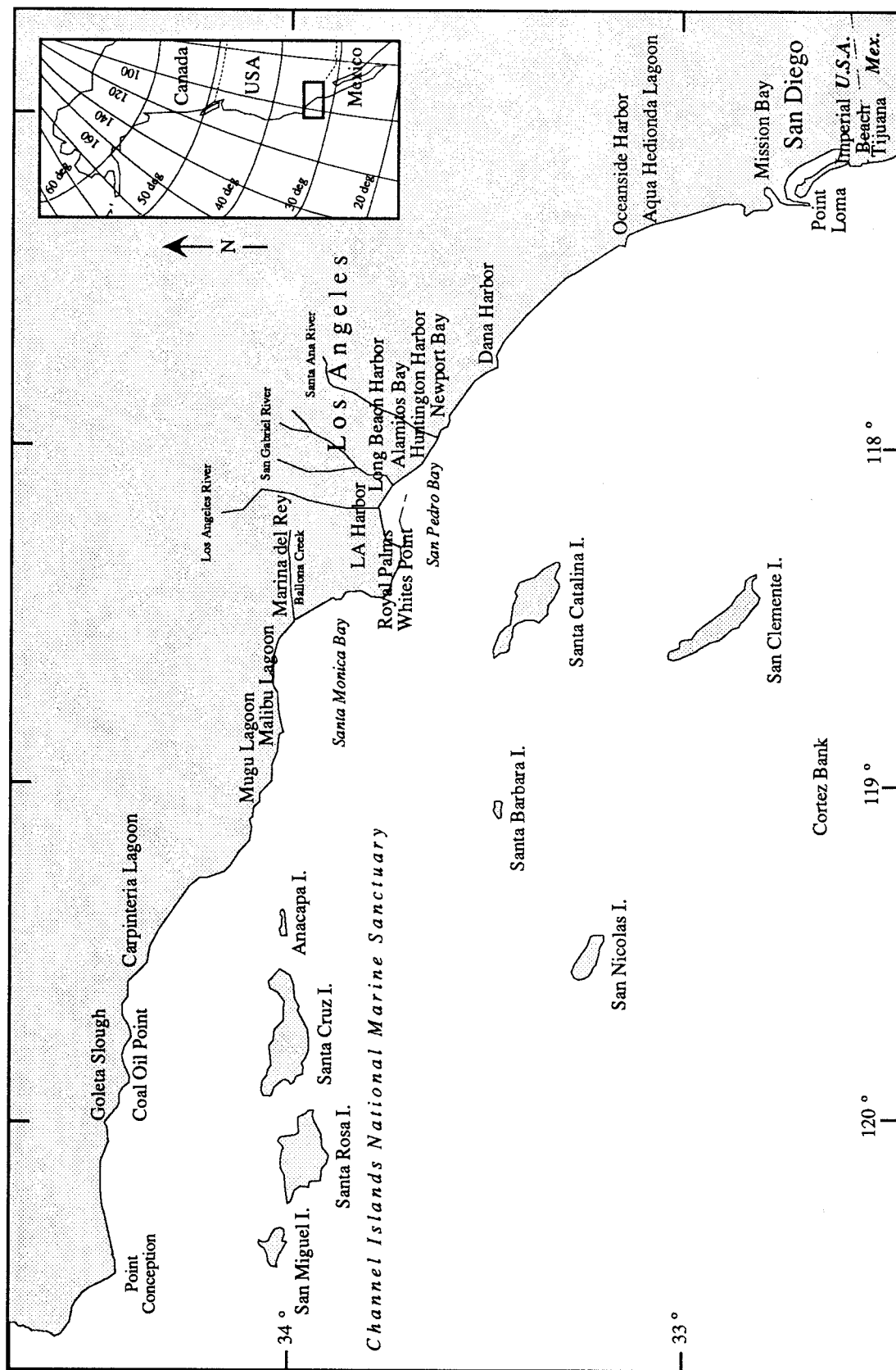
Figure 1.3. General map of the northern portion of the Southern California Bight showing bays, lagoons, and rivers cited in report.

BACKGROUND

The Southern California Bight: Geography and Perspective

It is impossible to evaluate contaminant trends and patterns without first understanding the geography and hydrography of the Southern California Bight. The Bight is a 100,000-square mile submerged continental borderland of the Pacific Ocean bounded on the north, east, and southeast by a large mountainous reach of the North American coastline extending from Point Conception, Santa Barbara County, California, south 575 kilometers (km) to Cabo Colnett, Baja California, Mexico. The west is bounded by the inner boundary of the southward flowing California Current and by the true outer edge of the continental shelf (Figure 1.1). The narrow, mountain-ringed drainage basin experiences a Mediterranean climate (dry summers and short, occasionally wet, high-run-off winters). The waters of the Bight overlay a submerged continental borderland of an alternating series of deep basins and surfacing mountain ranges that form offshore islands radiating over 100 km seaward from the Los Angeles area. However, the salient oceanographic feature of the Bight that distinguishes it from all coastal areas to the north and south is the eastward indentation of the coastline that allows for a northward flowing return eddy, the counterclockwise Southern California Gyre. As a result of this gyre, the Bight is an enclave of regionally specific populations of marine life, a trap for warm water, and a reservoir for materials entering from the land, air, and sea. It is chiefly this "stall" in the current systems of the Pacific, coupled with an adjacent urban population of 15 million, that creates concern about contaminant loading and pollution effects on a regionwide basis.

From a national perspective, the Southern California Bight is equivalent in scale and shape to the Mid-Atlantic Bight, which extends 600 km from Point Judith, Rhode Island south to Cape Henry, Virginia. However, there are many significant differences between the two regions: because of its great depths, the Southern California Bight contains over 10 times as much water as the Mid-Atlantic Bight, but it hosts half the human population (15 as compared to 30 million) and less than one tenth the river flow and basin drainage area. On a first approximation then, the Southern California Bight has the capacity for a considerably greater assimilation of pollutants than the Mid-Atlantic Bight.

The Coastal Shelf

The mainland coastal shelf of the Bight is divided into several geographically distinct units. These are the Santa Barbara Basin, Santa Monica Bay, the San Pedro Bay region (including Los Angeles-Long Beach harbors), Newport Bay, the San Diego Bay and coastal region, and the northern coast of Baja California, Mexico.

The Santa Barbara Basin is a large elliptical shaped embayment with the major axis extending 100 km from east to west. It is bounded on the north by the mountainous Santa Barbara coast and on the south by four Channel Islands (from west to east, San Miguel, Santa Rosa, Santa Cruz, and Anacapa). The channel has a wide opening to the Pacific Ocean on the west and a narrow opening to the Santa Monica Basin and Ventura County coastline on the east. The water in the bottom of the basin (500 meters [m]) is below sill depth and devoid of macroscopic organisms. As a result, sediments are deposited unmixed as annual layers allowing scientists to monitor annual deposition of sediment, chemicals, remains of fish, invertebrates, and plankton. The major human population center adjacent to the basin is the city of Santa Barbara. However, the protected and undeveloped shores of the Channel Islands host large populations of seals and sea lions (over 25,000, principally at San Miguel Island). The four Channel Islands, together with Santa Barbara Island to the southeast, are protected and managed under the joint NOAA-U.S. Fish and Wildlife Service Channel Islands National Marine Sanctuary.

Santa Monica Bay is an indentation of the Bight bounded on the north by Point Dume and on the southeast by Palos Verdes Point, a linear distance of 60 km[1]. The bay extends from the shoreline of Los

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[1]This definition of Santa Monica Bay differs from that used in the recent nomination of Santa Monica Bay to the National Estuarine Program. In that nomination, Santa Monica Bay is defined to include the Palos Verdes Shelf eastward to Point Fermin. However, physiographically and ecologically, these are distinct regions.

Angeles and the adjacent cities of Santa Monica, El Segundo, and Redondo Beach westward to depths greater than 500 m. It is intersected by two major submarine canyons: Santa Monica in the central bay, and Redondo along its southern edge and penetrating to within 100 m of the shoreline. Two principal inlets of Santa Monica Bay are Marina del Rey, the largest marina in the nation, and the adjoining wetlands of Ballona Creek and King Harbor. This shoreline is entirely within the County of Los Angeles. Santa Monica Bay is similar in surface area to Raritan Bay and New York Harbor but averages 20 times deeper.

The San Pedro Bay region, south and east of Santa Monica Bay, is essentially the submarine shelf bounded to the north by the Palos Verdes Peninsula, to the south by the Newport Submarine Canyon, and by the mainland shelf break extending 30 km seaward (south) of Long Beach (Figure 1.2). From west to east, the prominent features of concern in the San Pedro Bay area include the steep Palos Verdes shelf, the combined Los Angeles and Long Beach harbors inside a long breakwater, the mouth of the completely channelized Los Angeles River, and two prominent lagoon systems: Alamitos Bay north of and Anaheim Bay south of the mouth of the San Gabriel River. The San Pedro Bay shelf is equivalent in scale to the New York Bight Apex but averages twice the depth.

The San Diego region is the length of coastline from Point La Jolla south 50 km to the United States-Mexico International Boundary. From north to south, prominent features are the generally unrelieved coastline from Point La Jolla to Point Loma; shallow, but channelized San Diego Harbor with an entrance at Point Loma; the sweeping curve of San Diego Bay from Point Loma to the international boundary, and offshore the boundary of Los Islas Coronados (Mexico). Between Point La Jolla and Point Loma lie the inlets to Mission Bay and the San Diego River. To the south and near the U.S.-Mexico boundary is the entrance to the Tijuana River estuary, an area of extensive tideflats that drains run-off from the United States and the City of Tijuana in Baja California.

The southern section of the Bight extends along the rocky shoreline of northern Baja California over 100 km to Cabo Colnett. The shoreline is broken by a large embayment, Bahia de Todos Santos, near Ensenada (population 200,000).

Lagoons and Bays

Along the mainland coastal shelf of the Bight are over 30 bays, harbors, lagoons, and tidal marshes (Figure 1.3). An inlet between Newport Beach and Corona del Mar leads into Newport Bay, the largest lagoon system. Lower Newport Bay contains several islands and channels and its shoreline is surrounded by homes, docks, and boat maintenance facilities. A channel extends north into Upper Newport Bay, which has an undeveloped shoreline and several tidal channels leading to near-natural wetlands and marshes. Other lagoon systems include the Ballona Wetlands, Anaheim Bay, and the Tijuana estuary, other small systems such as Bolsa Bay in Orange County, Hedionda and Encinitas lagoons in San Diego County, and Bahia de Todos Santos near Ensenada.

Islands and Banks

Offshore of the mainland coast are three chains of offshore islands and submerged banks. The first is the chain composed of the Channel Islands off Ventura and Santa Barbara plus Santa Catalina Island and Los Coronados (10 to 40 km from shore). Their eastern shores face the mainland and are exposed to the same currents, whereas the western shores of the Channel Islands are exposed to a considerable amount of upwelling and water from the California Current. Seaward of these (60 to 80 km from shore) is a line of three islands including San Nicolas, Santa Barbara, and San Clemente. Beyond these, 80 to 120 km from shore, are shallow banks (Cortez and Tanner). These islands and banks are mainly exposed to the southward flowing California Current. Except for Santa Catalina Island, the islands are largely unpopulated. Military and missile tracking operations are conducted on San Clemente and San Nicolas islands.

Living Resources

Ecosystems of the Bight range from salt marshes in bays and lagoons to extensive deep basin meso- and bathy-pelagic fish communities. The principal pelagic food web flows from phytoplankton (*Ankistrodesonus falcaties*) and zooplankton (*Acartia californiensis*) populations to the northern anchovy (*Engraulis mordax*). The northern anchovy is the base of an extensive secondary food web dominated by sea

birds, Pacific (chub) mackerel (*Scomber japonicus*), Pacific bonito (*Sarda chiliensis*), California barracuda (*Sphyraena argentea*) and on to swordfish (*Xiphias gladius*), sharks, and marine mammals. During some periods, as in the 1920s, the Pacific sardine (*Sardinops caeruleus*) was the primary forage fish. Offshore soft- and rocky-bottom resources are dominated by rockfish, sea perch of many species and prawns and crabs. Principal inshore resources are bass, perch, California halibut (*Paralichthys californicus*), and several species of croakers. In contrast to the East and Gulf coasts, few southern California fish are dependent on estuaries, bays, or lagoons. Rocky subtidal shores host a wide range of harvestable shellfish, especially sea urchins, abalone, rock scallops, and shrimp. Six species of seals and sea lions, with a total population of over 25,000, maintain rookeries principally on San Miguel Island, but haul out at hundreds of sites on the mainland and other islands. Anacapa island is the primary breeding site for local population of the once-endangered brown pelican. Forests of giant kelp (*Macrocystis pyrifera*) ring the rocky shorelines and many are continually harvested. Shellfish mariculture operations are conducted off Santa Barbara and in Aqua Hedionda Lagoon

The use of living marine resources in the Bight is intense. Over 200 million pounds of fish are extracted each year. For example, during 1981-86, commercial fisherman landed an annual average of about 180 million pounds of pelagic fish (mackerel, anchovy, squid, and sardine) from California, most of which came from the Southern California Bight (computed from data in California Department of Fish and Game [CDF&G], 1988). During the same period, 1.5 million recreational anglers fished the Bight, spent 230 million dollars each year on 5.3 million fishing trips, and captured 14.2 million fish weighing an estimated 20.4 million pounds. The species caught most frequently included rockfish, Pacific mackerel, Pacific bonito, barred sand bass (*Paralabrax nebulifer*), white croaker (*Genyonemus lineatus*), kelp bass (*P. clathratus*), barred surfperch (*Amphistichus argenteus*), and yellow tail (*Seriola lalandei*) (Helvey *et al.*, 1987). These fisheries are not equally distributed throughout the Bight but are concentrated within 50 km of the Los Angeles area and close to the major sources of contaminants.

Climate and oceanographic events have a profound effect on these resources. For example, prolonged occurrence of warm water transported from the south by aperiodic large-magnitude El Nino events increase the diversity and abundance of pelagic fisheries, depress temperate species availability, and reduce kelp production.

CONTAMINANT SOURCES AND INPUTS

In addition to hosting a human population of over 15 million, southern California is now the largest commercial center on the eastern Pacific for manufacturing, and aerospace and petrochemical industries. There have been numerous opportunities for pollutants to be transported to marine waters through spills, sewage discharges, power plant cooling water discharges, industrial discharges, atmospheric fallout, and run-off from flood control channels.

In past decades, sewage outfalls have been considered the principal sources of contaminants to the Bight. By 1983-84, 13 treatment plants collected, treated, and discharged to the ocean much of the 1500 million gallons per day (MGD) of sewage (National Research Council [NRC], 1990). All is treated primary, secondary, and tertiary and discharged by seven public authorities in Ventura, Los Angeles, Orange, and San Diego counties. Ventura County discharges secondary-treated effluent 40-m deep off Oxnard. Santa Monica Bay receives treated wastewaters and, until recently, digested sludge, discharged from the Hyperion Treatment Plant through two ocean outfalls at 60-m deep, 8 km offshore and 100-m deep, 10 km offshore, respectively. In late 1987, sludge discharge to the Bay ceased, with the majority after that date going to landfill, crop soil amendment, and capping material for hazardous waste impoundments.

In 1984-85, the County Sanitation Districts of Los Angeles County (CSDLAC) were discharging treated wastewater through two ocean outfall diffusers located approximately 60-m deep and 3 to 4 km off Whites Point and Royal Palms State Park near the southern corner of the Palos Verdes Peninsula. The City of Los Angeles' Terminal Island Treatment Plant discharged secondary treated wastewater into Los Angeles Harbor. Under a U.S. Environmental Protection Agency (EPA) 301h "waiver" permit, a third major outfall, operated by the County Sanitation Districts of Orange County (CSDOC), was discharging primary and secondary treated wastewater through one ocean outfall diffuser located approximately 60-m deep and 8 km offshore of Huntington Beach and Newport. There are now no major municipal discharges into Mission Bay or San Diego Harbor, but industrial discharges and chemical and ore spills occur there

from time to time. In 1964 municipal discharges to the bay and harbor were diverted to the ocean. In 1984-85, the City of San Diego discharged primary-treated municipal waste through a 60-m deep ocean outfall diffuser located 3 km west of Point Loma.

Contaminant inputs from sewage discharges have decreased by as much as an order of magnitude during the past two decades (Schafer, 1989) and as a result, other sources are being recognized as of equal or greater importance. Sources like dredge material disposal, aerial fallout, and run-off. For example, San Diego Creek drains agriculture fields of the Irvine Ranch area into the uppermost reach of Newport Bay. In 1987, over 1 million cubic meters of sediments and marshes were dredged from Upper Newport Bay to help reopen sediment-clogged channels and maintain the wildlife sanctuary. The dredged material was disposed 5 km offshore in Newport Submarine Canyon south of the Orange County sewage outfall. These and other sources of contaminants are discussed in subsequent chapters.

Principal sources of pollutants to northern Baja California include sewage treatment plant discharge, an oil-burning power plant between Tijuana and Ensenada, and fish processing plants and port facilities in Ensenada.

STRATEGY AND APPROACH

Status: Geographic Patterns

The first objective for this report was to place recent measures of contaminants, including those from the NS&T Program, into a regionwide perspective with emphasis on determining where sediments, mussels, and fish are becoming contaminated and where they are not. The geographic and physical settings described above provide natural boundaries for organizing environmental quality information and for comparing regions. Geographic trends can be analyzed on several scales. For the Bight as a whole, there is a natural downcoast northwest-southeast geography for examining spatial trends along the shoreline. Alternately, trends can be examined away from shore by comparing coastal contamination to that at offshore islands.

Investigators have taken advantage of this geography to test for regional scale contaminant sources and distributions. The Southern California Coastal Water Research Project [SCCWRP] (1973) developed a regionwide transport model and confirmed its utility in identifying three classes of input nodes using results from synoptic surveys of contaminants in coastal mussels (*Mytilus californianus*). The distribution of dichlorodiphenylethylene (DDE) in mussels throughout the region closely matched a "point source" function centered in the Los Angeles area. By contrast, lead was distributed in mussels in a pattern that most closely resembled a "line source" function (for example, the entire mainland coast as a source, probably through aerial fallout). However, cadmium (Cd) did not match any regional source function tested (point source, run-off, or line source). These patterns, demonstrating regionwide contamination for some pollutants, prevailed in 1971. A major question is, to what extent does regionwide contamination occur today, and are there recent data available sufficient to test for patterns attributable to major point sources, line sources (aerial fallout), or run-off sources? This is a major underlying question of this report.

In this report, part of the assessment was focused on this larger scale geography, taking advantage of monitoring data at coastal outfall sites, large-scale coastal surveys along the mainland shelf, and offshore data provided by surveys at the various island sites. This information was then contrasted with comparable data from the principal bays and harbors.

Of particular interest is comparing contamination among various bays and harbors, coastal sites used for dumping and sewage discharge, and more remote sites at banks and islands. A great deal of publicity has been given over the past 20 years to conditions surrounding the five major open coastal sewage discharge sites, but very little to most of the region's bays, harbors, marinas, and islands. Thus, it is not clear, from this broader geographic perspective, which are currently the most contaminated sites or where further research and remediation are most needed. The NS&T Program samples only about two dozen locations in the Bight. While the results of these samplings may provide some perspective on regional contamination, their density is too low to be practical for comparing conditions among various bays, coastal sites, and islands. Although there have been numerous other contaminant surveys at many separate locations along the coast and in bays and harbors, the data remain scattered among individual agency reports and have not been brought together in one report.

Long-term Trends

The second objective was to determine long-term trends of commonly monitored chemical contaminants in sediments, mussels, other shellfish, and fish of the Bight. The primary intent of the NS&T Program sampling is to determine long-term trends, but data for doing so only exist for 4 or 5 years, hardly long enough to encompass the several-decades of changes that have taken place in the Bight. Monitoring of contaminants in the Southern California Bight has been underway for over 30 years. Some of the data on long-term trends of PCBs and chlorinated pesticides have been published in the scientific literature (Smokler *et al.*, 1979; Young, Heesen, and McDermott, 1980a and b) but many still remain in the form of agency reports, unpublished data sets, and unpublished manuscripts. In reviewing existing data and past summaries and assessments, it became apparent that a considerable amount of data has not been used in the evaluation of trends. As a consequence, knowledge about long-term trends in contamination appears to be fragmentary when, in fact, the possibility exists for a more complete record.

Contaminant inputs to the Bight from sewage has decreased dramatically since the early 1970s (SCCWRP, 1988). However, the opportunity remains to determine the extent to which contamination has also decreased in sediments and marine life on a regional basis. While contaminant trends in some open coastal areas have been well documented, trends within most bays, lagoons, and estuaries of the Bight have been poorly documented. Therefore, data was sought that would allow a compilation of trends in each geographic area.

Contaminants of Concern

As work proceeded, a third major objective emerged: to identify contaminants of most and least concern. It is this objective that dictated the organization of the report. The great amount of data and information reviewed presented an important opportunity to help answer this question for conditions as they exist in the Southern California Bight. Although similar to the process of ecological risk assessment, there are no real guidelines or framework for using field monitoring data alone to make such an assessment, so a strategy was devised. At the end of each chapter an attempt is made to evaluate the current importance of each contaminant based on a series of evaluation criteria outlined below. Then, at the end of this report, the results of these individual assessments are brought together in a table and compared.

The approach used here is based on the following premises, assumptions, and strategy. The primary premise is that each of the contaminants selected for review is a hazard (potential threat) under specific conditions that may or may not be met in the Bight. The primary assumption is that contaminants of most concern can be demonstrated to have all or most of the following properties: 1) accumulate to toxic levels in water or sediments, 2) accumulate to excess amounts in plants, invertebrates, or fish either to the detriment of the fish or at concentrations that pose risk to seafood consumers, 3) that biomagnify through marine food webs and 4) that have inputs that are increasing or expected to increase. The corollary is that contaminants of least concern are those that do few or none of these, with emphasis on lack of demonstrable bioaccumulation and toxicity. For example, while the input of some contaminants may be increasing, they may be of little concern because they never accumulate excessively in water, sediments, or biota. Likewise, a contaminant is of low concern if, although it is elevated in sediments (as compared to reference sites), it has not reached levels thought to be toxic and is not accumulating in marine organisms.

Each chapter in this report is organized in a consistent manner to help make a qualitative assessment of concern for each contaminant. First, trends in inputs are evaluated to determine direction of change (increasing or decreasing). In many cases this required considerable reconstruction of existing data and assumptions about inputs.

Next, concentrations in sediments at specific sites are evaluated to determine if they are in excess and, further, if they are approaching or exceeding potentially toxic levels in sediments. Concentrations in water were not reviewed.

Concentrations in tissues of target organisms were reviewed to determine if they are obviously elevated in some areas. Specific groups of target organisms are reviewed separately.

1. Accumulation in mussels.

Like most filter feeders, mussels are capable of concentrating contaminants from the water column. For nearly three decades mussels have been used as "sentinel" organisms and sampled or deployed to measure contaminants otherwise difficult or impossible to measure in the water.

2. Accumulation in tissues of seafood organisms:

    a. Bivalves other than mussels, as well as other sea food mollusks, crustaceans, and echinoderms are frequently examined for contaminants and may or may not demonstrate bioaccumulation depending on species and tissue examined.

    b. Muscle and other tissues of sharks, rays, and bony fishes may accumulate contaminants independent of sentinel organisms such as mussels. Some criteria are available for estimating potentially damaging excesses in seafood. Accumulation in liver tissue is also considered

3. Biomagnification.

Beyond the process of direct bioaccumulation, organisms may acquire contaminants from their food. To confirm that a pollutant is undergoing biomagnification it is necessary to document the food web leading to the target species and then measure contaminants in various representatives of that food web. If levels then increase, one cannot rule out that biomagnification is not occurring. If there is no increase, or if there is a decease, one can clearly rule out biomagnification. Fortunately, there is sufficient data from contaminated areas of the Bight to attempt this assessment.

Sediments, bivalve mollusks, and fish liver tissue have been the principal components for monitoring of contaminants by the NOAA NS&T Program and these were the primary substrates for which existing contaminant data were sought for this report. Sediment toxicity is of growing concern, so this factor was included in the assessment. In addition, local, state, and federal resource managers, as well as the general public, have been especially concerned about potentially hazardous concentrations of contaminants in other more widely consumed tissues and products of fish, sharks, crustaceans, echinoderms, and mollusks. A great deal of public apprehension about the disposal of wastes in the ocean is based on the assumption that biomagnification of organic and inorganic chemicals, which has been demonstrated in certain terrestrial, freshwater, and estuarine systems, also occurs in marine ecosystems. Some scientists have challenged this traditional concept by suggesting marine food webs are unstructured. Young et al. (1980; 1981a) and others have devised several measures of food chain or food web (trophic) structure and have applied them specifically to measuring the biomagnification potential of several marine ecosystems in the Southern California Bight. The approach could have national significance.

As noted above, the results of these assessments are summarized at the end of each chapter for each contaminant. The summaries are then brought together, compared, and discussed in the concluding chapter.

CHAPTER 2
METHODS

To prepare this report, it was necessary to conduct a regionwide data search, acquire appropriate data sets, organize them into readily accessible files, reassemble selected records into comparable units of time, geography, species, and tissue types, and then make comparisons among geographic regions and among various points in time. These steps are outlined in more detail below.

SCOPE

Contaminants initially selected for review included a suite of up to 19 PAH compounds, 17 trace elements, PCBs, and 15 historically important pesticides (Table 2.1). Constraints in resources required that the work be limited to fewer numbers of chemicals; these are noted in bold type in Table 2.1. However, a brief scan of selected data sets was done to identify all chemicals searched for and reported. The study was limited to the Southern California Bight. It was defined to include that portion of the Pacific Coast of North America extending from Point Conception, California, south to Cabo Colnett, Baja California, Mexico and seaward to the break of the mainland shelf (see Figure 1.1). Data were sought for all bays, lagoons, harbors, and estuaries, as well as from basins, islands, and the coastal shelf. However, most of the data was collected for the United States portion of the Bight (Point Conception to the U.S.-Mexico boundary).

The study was limited to invertebrates, fish, and sediments. Data were not otherwise limited by tissue type, collecting methods, or chemical extraction and analytical techniques.

DATA COLLECTION AND PROCESSING

The southern California data search was conducted as part of a nationwide data search. Active data collection began in 1984, leading to a report on trends in PCBs and DDT along the U.S. Pacific Coast (Matta et al., 1986). Active collection continued through January 1988.

Original concentration values for individual samples or composites were sought. If individual values were omitted from published reports, authors or performing laboratories were requested to locate and submit values for individual data points. In addition to the contaminant values, data and auxiliary information on sampling and analytical procedures were sought and collected in any available form including published and unpublished reports, memos, laboratory records, raw data sheets, and magnetic tapes and diskettes.

For the purpose of data inventory, basic information about data sets was extracted into simple worksheet and bibliographic systems. The extracted information included survey name, start and end dates; name of principal investigator and performing agency; name, location, and coordinates of sampling sites; primary taxa or substrates and tissues analyzed; number of samples and/or composites; and lists of target analytes. Data on contaminant concentrations, sample and sampling characteristics, and analytical methods were extracted into a common format and then entered into desktop computer data base management systems specifically developed for this purpose (Buchman, 1986; NOAA, 1986).

Table 2-1. Variables measured as part of the NS&T Program. Chemicals and metals in bold type are explicitly reviewed in this report.

Chlorinated Synthetic Organics	Polycyclic Aromatic Hydrocarbons (PAH)	Elements	Other Variables
Aldrin	Acenaphthene	Aluminum	Fish length, weight, sex
Alpha-chlordane	Anthracene	Antimony	PAH metabolites in fish bile
o,p'-DDD	Benz(a)anthracene	**Arsenic (As)**	
p,p'-DDD	Benzo(a)pyrene	**Cadmium (Cd)**	Sediment grain size
o,p'-DDE	Benzo(a)pyrene	**Chromium (Cr)**	Sediment total organic carbon
p,p'-DDE	Biphenyl	**Copper (Cu)**	
o,p'-DDT	Chrysene	Iron	
p,p'-DDT	Dibenz(a,h)anthracene	**Lead (Pb)**	
Dieldrin	2.6-Dimethylnaphathalene	Manganese	
Endrin	Fluoranthene	**Mercury (Hg)**	
Heptachlor	Fluorene	Nickel	
Heptachlor epoxide	1-Methylnaphthalene	**Selemium (Se)**	
Hexachlorobenzene	2-Methylnaphthalene	Silicon	
Lindane (gamma-BHC)	1-Methylphenanthrene	**Silver (Ag)**	
Mirex	Phenanthrene	**Tin (Sn)**	
Trans-nonachlor	Perylene	**Zinc (Zn)**	
	Pyrene		

PCBs

    Dichlorobiphenyls
    Trichlorobiphenyls
    Tetrachlorabiphenyls
    Pentachlorobiphenyls
    Hexachlorobiphenyls
    Heptachlorobiphenyls
    Octachlorobiphenyls
    Nonachlorobiphenyls
    18 individual congeners

DATA ANALYSIS

For analysis of trends and geographic distributions, data were always sorted by survey date, taxonomic categories, tissue types, and performing laboratory. Tissue types distinguished for this report were: whole organism, muscle or flesh, liver, and gonad. To calculate mean values, detection limits were halved when contaminants were listed as not detected although better methods of handling these values exist (Helsel, 1990).

Some assessment of data quality was attempted. For older surveys however, insufficient information was available to determine confidence in results. Subtle differences in methods can affect results (D'Elia et al., 1989). Lowering of detection limits and improvements in separation and cleanup techniques have increased confidence in results of analyses over time. Further improvements in methods would be helpful. In a recent survey of contaminants present in wastewater effluent, 91 compounds were detected but not characterized by traditional gas chromatography/mass spectrometry (GC/MS) methods (Clark et al., 1991). When the same effluent was analyzed using liquid chromatography/mass spectrometry, an additional 95 compounds were quantified, 20 of which had known carcinogenic or genotoxic activity.

DATA PRESENTATION

The principal analysis products developed for this report were maps and graphs designed to reveal the spatial and temporal variations of contaminant levels and the abundance or paucity of data at various localities and time periods. Individual or site mean concentrations were generally plotted as bars using scales that encompassed most of the data points. Uniform scales were used wherever possible to encourage direct comparisons. However, the reader is cautioned to note scale on each figure, as use of uniform scales was not always possible.

Means, medians, ranges, and standard deviations of contaminant concentrations in sediments, mussels, fish, and other species were computed and listed for individual surveys, geographic region, time periods, species, and tissues. Geographic differences among bays and other survey units were further revealed by tabulating and comparing median values and noting apparent differences. Although transplanted mussels have been analyzed for contaminant accumulations, only analyses of resident populations were included in this report. Mussel species are designated here as *Mytilus californianus* and *Mytilus edulis*, according to traditional practice. However, according to McDonald and Koehn (1988) the species commonly referred to as *M. edulis* is probably actually *M. galloprovincialis* in southern California.

In most cases, data from different surveys were plotted separately. In some cases, however, data from several surveys were plotted together on the same charts. Where this was done, data sources were clearly identified.

All fish and macroinvertebrate data are presented in units of parts per million wet weight (ppm ww) in keeping with older historical conventions and to help in evaluating significance of concentrations relative to existing and proposed seafood and predator protection quality criteria. In contrast, all sediment and most mussel concentrations were reported here as ppm on a dry weight (dw) basis in keeping with past protocols. Parts per million is equivalent to milligrams per kilogram (mg/kg) and micrograms per gram (μg/g).

More specific details of data presentation and analysis are presented with the findings in subsequent chapters.

COMPARISON TO CRITERIA

It is useful and important to compare contaminant concentrations with levels of concern. There are currently no widely accepted criteria for establishing regulatory concentrations of concern in sediments. To provide informal guidelines for use in the evaluation of data from the NS&T Program, Long and Morgan (1990) examined data from a number of different technical approaches and geographic locations and determined the ranges in chemical concentrations often associated with toxic effects. For each of a number of trace metals and organic compounds, they determined Effects Range-Low (ER-L) and Effects Range-Median (ER-M) values. The ER-L values were interpreted as being the concentrations at which toxic effects may first be observed. The ER-M values were interpreted as the concentrations often or always associated with toxic effects in a number of independent studies.

Further, no criteria have been proposed that indicate tissue concentrations that are hazardous to organisms bearing those concentrations. However, there do exist a suite of enforceable "action limits" and proposed criteria for the protection of human and wildlife consumers of organisms contaminated with PCBs or chlorinated pesticides. The only standards that are federally enforced are the U.S. Food and Drug Administration (FDA) "action limits," used to prevent interstate sale of contaminated seafood. The action-limit values range from 0.1 ppm ww for mirex to 5.0 ppm ww for DDT and toxaphene (Table 2.2). Other nations have similar, equivalent, or more restrictive action limits (Nauen, 1983).

Table 2.2 Summary of action limits and proposed criteria (in ppm ww) for PCBs and pesticides in fish or shellfish.

Chemical	FDA Action Limit	NSSP Shellfish	Predator Protection Levels NAS[d] Aquatic Wildlife	NAS[e] Marine Wildlife
Aldrin	0.30	0.20[a]	0.10[b]	f
Dieldrin	0.30	0.20[a]	0.10[b]	f
Endrin	0.30	0.20[a]	0.10[b]	f
DDT				
DDE				
DDD (TDE)				
Total DDT	5.0	1.5	1.0	0.05
Chlordane	0.3	0.03	0.10[b]	0.05
Heptachlor	0.3	0.20[a]	0.10[b]	0.05
Heptachlor epoxide		0.20[a]		
Lindane		0.20	0.10[bf]	0.05
BHC (other than lindane)		0.20		
Methoxychlor		0.20		0.05
Endosulfan			0.10[b]	0.05
Mirex	0.1			0.05
Kepone	0.4 crabs 0.3 fish, shellfish			
Toxaphene	5.0		0.10[b]	0.05
HCB			0.1	0.05
2,4-D		0.50		
PCBs[h]	2.0		0.5[c]	0.5[g]

[a] "Alert" level if combined value of the five pesticides exceeds 0.20 ppm ww; shellfish bed should be closed if combined values exceed 0.25 ppm ww. (NAS, 1974).

[b] Singly or in combination with others listed. (NAS, 1974).

[c] NAS, 1974

[d] In whole fish. (NAS).

[e] Homogenate of at least 25 fish of appropriate size and species. (NAS, 1974).

[f] Sum of these four pesticides should not exceed 0.005 ppm ww. (NAS, 1974).

[g] Add all Aroclors for total. (NAS, 1974).

[h] Measured as Aroclors.

There also exist proposed criteria for protecting humans and/or wildlife from effects of pesticides and PCBs, including numerical concentration values for U.S. FDA-designated "warning" levels of excessive contamination of shellfish. These values, proposed by the National Shellfish Sanitation Program (NSSP) range from 0.03 ppm ww for chlordane to 1.5 ppm ww for total DDT (tDDT) (National Academy of Sciences (NAS), 1974). Further, NAS (1974) also recommended numerical criteria for concentrations of contaminants in fish for protection of predatory wildlife. For freshwater fish, these concentration levels ranged from 0.1 ppm ww for nine pesticides to 1.0 ppm ww for DDT (Table 2.2). For protecting predators of marine fish, even more restrictive criteria were proposed by NAS (1974). These range from 0.005 ppm ww for the sum of dieldrin, aldrin, endrin, and heptachlor epoxide to 0.05 ppm ww for tDDT (Table 2.2). These values have not been adopted as federal regulatory standards, but are frequently cited in state programs.

The U.S. FDA has no action limits for trace metals other than mercury (Hg; 1.0 ppm ww). However, the California Department of Health Services (CDHS) has set a health advisory level of 0.5 ppm ww for total mercury in the edible portion of sport-caught fish and shellfish. If the mercury content of fish or shellfish regularly exceeds this level, CDHS may issue a health advisory warning against consumption of contaminated species in specific locations (Hayes and Phillips, 1987). For some of the remaining metals, useful reference values may be the calculated median values of the standards that have been set by other countries (Table 2.3). These median international standards are not enforceable in the United States, but they do give an indication of what other countries have decided are undesirable concentrations of trace elements in shellfish (Nauen, 1983). Also included in Table 2.3 are median international standards for pesticides reviewed in this report.

In addition, models now exist for computing incremental risk of cancer in humans given specified seafood consumption rates and contaminant concentrations. All these existing U.S. FDA action limits and proposed tissue concentration criteria are for the protection of human or wildlife consumers of marine and aquatic animals, not for the protection of the contaminated fish or invertebrates themselves.

Table 2.3. Median international standards for contaminants in shellfish.

Contaminant	Median standard (ppm wet weight)	Range	Number of countries with a standard
Elements			
Arsenic	1.4	0.1-5.0	10
Cadmium	1.0	0.1-2.0	5
Chromium	1.0	–	1
Copper	20	10 - 30	6
Lead	2.0	1.0-6.0	10
Mercury	0.5	0.1-1.0	10
Selenium	0.3	–	1
Silver	None	–	--
Zinc	70	40-100	2
Tin	175	50-250	12*
Pesticides			
DDT	5	2.0-5.0	7*
DDT, fish liver	5	5.0-5.0	2*
PCB	2	1.0-5.0	6*
PCB, fish liver	15	5.0-25.0	2*
Chlordane	0.1	0.01-.03	3*
Dieldrin	0.4	0.1-1.0	4*

* Computed directly from Nauen (1983); all others from Hayes and Phillips (1987).

CHAPTER 3
SURVEY HISTORY AND DISTRIBUTION OF DATA (INVENTORY)

Over 18 million dollars are spent annually on marine monitoring in the Southern California Bight (National Research Council (NRC), 1990) As a result, there exists a large and diverse data base. At least 150 local, state, and federal surveys have been conducted to measure contaminants in sediments, invertebrates, and fish since the early 1960s. The number of sediment samples is estimated to be in the range of 6000 to 8000. Samples of marine life for tissue analysis are also in the range of 6000 to 8000. For organic chemicals alone the estimate is about 5000, of which 4500 have been extracted and entered into NOAA's data base systems (Figure 3.1).

The history of sampling that generated these data are reviewed below. The data sets actually used in this report are identified and the distribution of these data among geographic areas, time periods, and species is described.

SURVEY HISTORY

In order to evaluate the historical data, it is important to be aware of the history of principal surveys and the methods, species, and collecting sites. The history of principle survey activities frequently referred to in subsequent chapters is outlined below.

Sediment Surveys

The coast of southern California has been extensively surveyed for trace chemicals in surface sediments and in cores. Surface sediment sample data reveal recent contamination conditions whereas cores, and in particular dated cores, reveal contamination trends over many years, decades, and in several cases, centuries.

Prior to 1960, over 5000 samples were taken and analyzed to reveal the complexity, organic content, and mineralogy of shelf and basin sediments. Data on 20 trace elements, naphthalenes, and aromatic and aliphatic hydrocarbons in specific shelf and basin areas are summarized in Emery (1960).

The history of sediment sampling and monitoring in connection with pollution assessments began in 1969 when Klein and Goldberg (1970) measured mercury in sediment samples from sites in Santa Monica Bay and along the Palos Verdes Peninsula. In 1970 and 1971, SCCWRP conducted and/or sponsored sediment surveys at sites around all five major coastal discharge sites including Oxnard/Port Hueneme, Santa Monica Bay, Palos Verdes, Orange County, and Point Loma (SCCWRP, 1973; Eganhouse et al., 1976). From these surveys, Galloway (1972a and b; 1979) analyzed spatial patterns for 10 trace elements not including mercury while Young, McDermott, and Heesen (1976b) reported results for PCBs and DDT compounds. Mercury analyses were subsequently performed on these and other Santa Monica Bay and Palos Verdes samples collected in 1972 (Eganhouse et al., 1976). DDT was also measured at several sites in 1971 (Anderson et al., 1982).

In 1973, MacGregor (1976) analyzed DDT compounds in sediments from a series of transects across the Santa Monica and San Pedro coastal shelves and basins, seaward to Santa Catalina Island. During the same year, Chen and Lu (1974) analyzed for trace metals and organochlorine compounds in surface and subsurface sediments at a similar grid of the sites across the San Pedro Basin as well as within Los Angeles - Long Beach harbors.

By 1973-74, near-routine sediment chemistry monitoring surveys were underway by public agencies at several points along the coast including Port Hueneme/Oxnard (Marine Biological Consultants [MBC] Inc., 1974, Environmental Quality Analysts, Inc. and MBC, 1975), Santa Monica Bay (Hyperion Treatment Plant, unpublished data), Palos Verdes (CSDLAC, unpublished data; CSDLAC, 1981; Smith and Green, 1976), Los Angeles-Long Beach harbors (Chen and Lu, 1974), Orange County (CSDOC 1974, 1975, 1976, 1977, 1978, 1979, 1980, 1981, 1982, 1983, 1984, 1985, 1986; Greene, 1976), and Point Loma (City of San Diego, unpublished data). Sometime prior to 1975, Salas Flores et al. (1975) conducted a survey of nickel (Ni) and vanadium (V) in oiled sediments along the northern coast of Baja California between the United States-Mexico border and Ensenada to determine the distribution of oil from Mexican oil spills and seepage. The survey involved 70 samples at 25 sites.
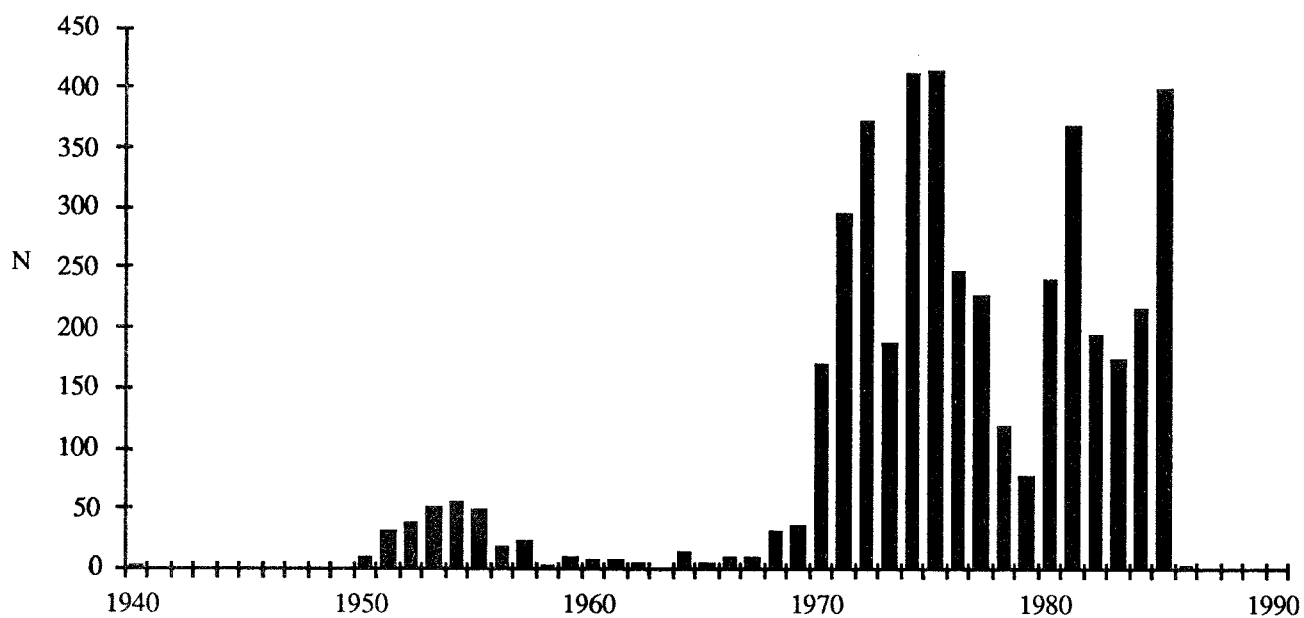
Figure 3.1. Long-term variation in number (N) of biological samples analyzed for chlorinated hydrocarbons.

In 1976 and 1977, U.S. Minerals Management Service (MMS; formerly the Bureau of Land Management, [BLM]) sponsored several major surveys of sediment chemistry including both trace elements and organic chemicals at over 700 sites throughout the Bight. Portions of these data (for example, barium (Ba); Chow et al., 1978) were published, but the majority have not been. At the same time, SCCWRP conducted a survey at 70 sites along the 60-m isobath between Point Conception and the United States-Mexico border (Word and Mearns, 1979). This, and previous data sets, were reviewed by Katz and Kaplan (1981). Shelf sampling expanded further with a sediment survey at up to five depth zones between Point Dume and Dana Point and along the Point Loma coast (Bascom, 1978; Jan and Hershelman, 1980; Hershelman et al., 1981). The shelf survey was extended westward to Port Hueneme in 1980 (Hershelman et al., 1982), but many of the data on trace metals remains unpublished.

In addition to these routine and synoptic surveys, various smaller municipalities began contracting sediment chemistry surveys including sites at Montecito near Santa Barbara (MBC, 1973), San Elijo near Oceanside (SCCWRP, 1982) Newport Bay (Young et al., 1975; MBC and SCCWRP, 1980; and Liu and Schneider, 1988), and in San Diego Harbor (Young et al., 1975; Ladd et al, 1984). By the mid-1980s, sediment chemistry surveys were underway or had been conducted at additional deepwater sites off Point Dume and Orange County (Thompson et al., 1984; 1986), at proposed dredge dumpsites (Tetra Tech and MBC, 1985), and in several bays and harbors including Marina del Rey (Soule and Oguri, 1980b; 1985; 1986; 1987), Newport Bay (Orange County Environmental Management Agency [OCEMA], 1986; 1989), San Diego Harbor (Young et al., 1975; Ladd et al., 1984), in the Tijuana River estuary (Gersberg et al., 1989), and at NOAA NS&T sites (Malins et al., 1987; NOAA, 1987a and b; NOAA, 1988). In 1985, Thompson et al., (1987) repeated sampling at many of the reference sites previously sampled in the SCCWRP 60-m survey, including for the first time, analyses of PAHs. A coincident (1985) survey in bays and near coastal waters was focused exclusively on PAHs (Anderson and Gossett, 1986). At that time there was mounting survey activity for organotins, especially in San Diego Harbor (as reviewed in Salazar et al., 1987). Contaminant monitoring increased substantially in Santa Monica Bay in the 1980s (City of Los Angeles, 1982; 1983; 1984).

Long-term histories of sediment contamination by trace elements and chlorinated hydrocarbon have also been developed from core samples taken in the anaerobic Santa Barbara Basin off Santa Barbara in 1971 (Young et al., 1973a; Bruland et al., 1974; Chow et al., 1973; Hom et al., 1974), during the mid-1970s (Ng and Patterson, 1982; Kettenring, 1981), and again in the 1980s (Schmidt and Reimers, 1987; Finney and Huh, 1989), and at the Palos Verdes Peninsula (Bascom et al., 1982; Stull et al., 1986).

As a result of these surveys, there is a data base for an estimated 6000 to 8000 samples for trace contaminants in sediments from the Southern California Bight, with surficial samples covering the period 1969 to present and core samples extending the record backwards five to ten decades.

From this sampling history, we reviewed data in detail from the nine regionwide surveys described in Table 3.1 plus selected data sets described above from specific embayments including Marina del Rey, Los Angeles-Long Beach harbors, Newport Bay, and San Diego Harbor.

Mussel Watch Surveys

Mussels and other bivalve mollusks concentrate many contaminants from seawater. There is a long history of "Mussel Watch" surveys in the Southern California Bight. Surveys of contaminants in bivalves began in 1963-64 when Young and Folsom (1973) analyzed for three radionuclides (^{50}Mn, ^{60}Co, and ^{55}Zn) in mussels from 12 sites between Point Conception, California and Punta Banda, Baja California. In 1967, the National Pesticide Monitoring Program (NPMP) began monthly sampling for organochlorine residues in M. edulis at three southern California sites as part of a 180-station network (Butler, 1973). The sites were at Point Mugu Lagoon, Ventura County; Anaheim Bay, Orange County; and in Agua Hedionda Lagoon in San Diego County. Sampling frequency shifted from monthly to quarterly or less in 1968 and terminated in May 1972. However, all three sites were reoccupied twice in 1977 (Butler et al., 1978).

In the summer of 1971, SCCWRP conducted a survey of M. californianus at 20 sites between Point Sal (Santa Barbara County, California) and Punta Banda (Baja California, Mexico). Samples were analyzed for radionuclides (Young and Folsom 1973), DDT and PCB compounds (SCCWRP, 1973; Risebrough et al., 1976; Young et al., 1973), and at least 12 trace elements (SCCWRP, 1973; Alexander and Young, 1976; Alexander et al., 1976). Whole soft tissue was analyzed for chlorinated hydrocarbons and four separate organs were analyzed for trace elements.

Table 3.1. Principal regionwide surveys of contaminants in sediments of the Southern California Bight, 1969 through 1986.

Survey Period	Name of Survey	Areas Surveyed	Analytes	Number of Stations	References
1969	Klein and Goldberg Mercury Survey	Palos Verdes, Santa Monica Bay	Hg	21	1
1970-71	SCCWRP 5-Outfall Surveys	Oxnard, Santa Monica Bay, Palos Verdes Orange County, Point Loma	10 metals, DDT PCBs, Hg		2
1973	San Pedro Bay and Basin Survey	Los Angeles-Long Beach harbors, San Pedro Bay and basin; Santa Catalina Island	9 metals, DDT PCBs, dieldrin,	20	3
1977	60-Meter Survey	Point Conception to U.S.-Mexico boundary; 60-meters	7 metals, DDT, PCBs	71	4
1977-78	SCCWRP Shelf Survey	Point Dume to Dana Point 20 to 700 meters	9 metals	148	5
1978	Los Angeles-Long Beach Harbor Survey	Point Dume to Dana Point; 20 to 700 meters	9 metals, DDT, PCBs		6
1980	Point Dume to Port Hueneme Survey	Point Dume to Port Hueneme 15 to 750 meters	7 metals	73	7
1985	Reference Survey	Point Conception to U.S.-Mexico boundary; 30, 60, and 150 meters	7 metals, DDT PCBs, PAHs	38	8
1985	SCCWRP PAH Survey	Santa Monica Bay to San Diego Harbor	PAHs		9
1986-present	NOAA NS&T Mussel Watch	Coal Oil Point to Tijuana	17 metals, PAHs, PCBs, 15 pesticides		10

1. Klein and Goldberg, 1970.
2. SCCWRP, 1973; Galloway, 1972a and b ; Eganhouse et al., 1976
3. Chen and Lu, 1974.
4. Word and Mearns, 1979; Mearns and Young, 1983.
5. SCCWRP, unpublished data

6. Soule and Oguri, 1980a
7. Hershelman et al., 1982
8. Thompson et al., 1987
9. Anderson and Gosset, 1986
10. NOAA, 1987; NOAA, 1988

During 1972-73, Chow *et al.* (1976) conducted a survey of lead and lead isotopes in *M. edulis* and *M. Californianus* at 19 sites between Point Piedras Blancas, in central California, and Punta Banda in Baja California, including 15 sites in the Southern California Bight.

The resolution of chemical patterns along the Mexican coast was increased in July 1973 when Suarez Vidal and Acosta Ruiz (1976a and b) measured DDT, copper (Cu), and zinc (Zn) in *M. californianus* from 10 to 11 stations located between Punta Bandera and Punta Banda, Baja California

During 1974, SCCWRP resampled many of the southern California sites surveyed in 1971 (deLappe *et al.*, 1980). Composites of whole tissue were analyzed for DDT and PCBs by Risebrough and deLappe and total mercury in composites of each of three organs by Eganhouse. Other trace elements were not analyzed. In addition, Dunn and Young (1976) sampled *M. edulis* and *M. californianus* from 19 mainland and 6 island stations for the aromatic hydrocarbon, benzo(a)pyrene (B(a)P). Total mercury was also determined and reported by Eganhouse *et al.* (1976).

Also during 1974, Young, Heesen, and McDermott (1976) deployed *M. californianus* in cages at five depths to record PCB and DDT uptake off Palos Verdes. Total exposure was 13 weeks. Later, mussels were also deployed in Santa Monica Bay, near the Orange County outfall, and off Point Loma.

A bivalve survey in harbors was also conducted in 1974. In January 1974, SCCWRP sampled *M. edulis* at 15 harbor and coastal sites between Royal Palms and San Diego. Six samples of whole, soft tissue were composited and analyzed for PCB 1254 at each site. Digestive glands were removed from six more mussels at each site and analyzed individually for 25 trace elements using optical emission spectrometry (OES). Remaining organs (gonad, muscle, and "other tissue") were removed from 10 males and 1 female at each site and analyzed for 25 trace elements, also by OES (Young *et al.*, 1975)

In 1975, Moss Landing Marine Laboratory (MLML) collected ten replicate samples of *M. californianus* from a Santa Catalina Island site and analyzed them to determine variability for nine trace elements (Ag, Al, Cd, Cr, Cu, Mn, Ni, and Pb).

During 1975-76, six intertidal and six benthic invertebrate species were collected as part of the BLM surveys and analyzed for eight trace elements (Ba, Cd, Cr, Cu, Ni, Pb, V, and Zn; Martin *et al.*, 1978). Included were collections of *M. californianus* from four coastal sites (Coal Oil Point, Palos Verdes, Corona del Mar, and San Diego pier), an offshore oil platform (Heidi), and six islands (Santa Catalina, Santa Barbara, San Nicolas, San Clemente, San Miguel, and Santa Cruz).

From 1976 through 1978, *M. edulis* and *M. californianus* were collected from 18 sites in central and southern California and analyzed for four classes of trace contaminants as part of the U. S. Mussel Watch (Farrington *et al.*, 1983; Goldberg *et al.*, 1978). PCBs, DDE, and aromatic hydrocarbons were measured in composites of whole tissue and juice from at least 25 individuals per site in 1976 and 1977 (Farrington *et al.*, 1982 and 1983). Six trace metals (Ag, Cd, Cu, Ni, Pb, and Zn) and two radionuclides (Pu and Am) were measured in composites of whole tissue from five organisms in 1976 and ten each in 1977 and 1978 (Goldberg *et al.*, 1978 and 1983).

Also, as noted above, during 1977, the NPMP twice reoccupied three previously monitored sites (1967-72) measuring PCBs and chlorinated pesticides (Butler *et al.*, 1978).

Surveys along the Mexican coast of the Bight resumed in 1977. Between May and December 1977, Cajal-Medrano and Gutierrez-Galindo (1981) monitored monthly changes of six DDT metabolites in composites of Pacific and European oysters *Crassostrea gigas* and *Ostrea edulis* from culture operation at Punta Banda and Bahia San Quintin. Coastal mussels were sampled from September 1977 to January 1978. Resident mussels were sampled at four sites between Tijuana and Erendira and buoyed mussels at three sites between Bahia de Todos Santos and Bahia San Quintin (Gutierrez-Galindo, 1980; Gutierrez-Galindo and Cajal Medrano, 1981).

The first sampling of *M. californianus* by the California Mussel Watch (CMW) also occurred in 1977. Of 32 statewide stations sampled in July and November 1977, there were 3 in central California, 7 along the southern California mainland coast, and 7 on five offshore islands (Stephenson *et al.* 1979a and b). These sites were resampled in August and November-December 1978 for 11 trace elements (Ag, Al, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn). Triplicate determinations were made from single composites of whole, soft

tissue from 45 specimens (split into three groups of 15 each, Flegal *et al.* (1981). For PCBs, DDTs, chlordane, other pesticides, aromatic hydrocarbons, and dioxins (TCDD), replicate determinations were made on composites of whole, soft tissue from at least 40 mussels (Risebrough *et al.* 1980). De Lappe *et al* (1980) compared trends at reoccupied sites between 1971 and 1977.

In January 1977 and April 1978, replicate samples of *M. californianus* were taken from Government Point near Point Conception and Coal Oil Point, Santa Barbara County to determine variability in concentrations of eight trace elements (Al, Cd, Cr, Cu, Fe, Ni, Pb, and Zn) as part of a BLM Outer Continental Shelf (OCS) survey (Gordon *et al.*, 1980).

The CMW Program continued with a variety of activities from 1979 to 1985 including use of resident and transplanted *M. edulis* and initiation of intensive surveys in bays at the expense of repeated sampling at the 32 original sites (Phillips, 1988). Details of each annual activity are summarized in subsequent annual reports (Stephenson *et al.,* 1979; 1980a and b, 1986; State Water Resource Control Board (SWRCB), 1982; Hayes *et al.*, 1985; Hayes and Phillips, 1986 and 1987; Ladd *et al.,* 1984). Intensive surveys were conducted in Santa Monica Bay in 1980, Los Angeles-Long Beach harbors in 1982, and San Diego Harbor in 1983.

After a 4-year interval, *M. californianus* were resampled in 1982 along the Mexican coast of the Bight. Samples were taken approximately monthly from February to September at eight sites between Punta Bandera and off Bahia de San Quintin and analyzed for the PCB Aroclor 1254 (Gutierrez-Galindo *et al.,* 1983a; Sanudo Wilhelmy, 1983) and for organochlorine pesticides including DDT metabolites, heptachlor, heptachlor epoxide, and aldrin (Gutierrez-Galindo *et al.,* 1983b). Samples from three of these 1982 sites were also analyzed for eight trace elements. Mexican Mussel Watch sampling intensified to include a survey of silver as far south as Punta Eugenia (Martin *et al.*, 1988), a survey of mercury (Gutierrez-Galindo and Flores Munoz, 1986) and special surveys of DDT in clams (*Tivela stultorum*; Flores-Baez *et al.*, 1987) and oysters (*C. gigas*; Gutierrez-Galindo *et al.*, 1984) in Bahia San Quintin.

During 1984, Green *et al.* (1986) compared transplanted mussels and water samples for 13 chlorinated hydrocarbon compounds. Data are presented for both the Bodega Head control site and a site at the Whites Point outfall at Palos Verdes. During 1985, the Los Angeles Regional Water Quality Control Board (LARWQCB) sponsored a survey of chlorinated hydrocarbons and PAHs in bivalves from many of the mussel watch sites sampled during 1971 by SCCWRP (Risebrough, 1987).

In the winter of 1987, Science Applications International Corporation (SAIC) as part of the NOAA NS&T Mussel Watch Project, began an annual survey of *M. edulis* or *M. californianus* at 12 coastal, 2 harbor, and 2 island sites in southern California. Triplicate composites of whole, soft tissue were analyzed for 17 trace elements, PCBs (by chlorination number), 16 chlorinated pesticide compounds, and 19 PAHs. Triplicate sediment samples were also taken nearby (Boehm *et al.*, 1987). PCB analyses are now conducted for 18 individual congeners and converted to an estimate of tPCBs using results of dual analyses of 302 samples (NOAA, 1989).

Data selected for detailed review in this paper are from the 11 surveys cited in Table 3.2, including the 1971 and 1974 SCCWRP surveys, the 1977 through 1985 CMW surveys (resident mussels only), the 1976-77 U.S. Environmental Protection Agency (EPA) Mussel Watch Survey, and the 1986 NOAA Mussel Watch Survey.

Table 3.2. Principal regionwide surveys of contaminants in mussels of the Southern California Bight, 1966 through 1986.

Survey Period	Name of Survey	Areas Surveyed	Analytes	Number of Stations	References
1971	Coastal Mussel Survey	Gaviota to Point Loma, 6 islands	7 trace elements, DDT, PCBs	17	2
1966-72	National Pesticide Monitoring Program	Point Mugu, Anaheim Bay, Hedionda Lagoon	15 organochlorine compounds	3	1
1972-73	Chow Lead Survey	Gaviota to Punta Banda	Pb	15	3
1974	Coastal Mussel Survey	Point Conception to Point Loma/ La Jolla, 8 islands	p,p'-DDE, PCBs	22	4
1974	Harbor Mussel Survey	Los Angeles-Long Beach harbors, Newport Bay, and San Diego Harbor	8 trace elements, Aroclor 1254	15	5
1974	Mussel B[a]P survey	Gaviota to Sunset Cliffs, 6 islands	Benzo[a]pyrene	25	6
1974	Mussel Mercury Survey	Gaviota to San Diego, 5 islands	Hg, organic Hg	19	7
1976-78	EPA Mussel Watch Program	Rincon Cliffs to San Diego Harbor	8 trace elements, DDTs, PCBs, other chlorinateds, PAHs, radionuclides	7	8
1977	National Pesticide Monitoring Program	Point Mugu, Anaheim Bay, Hedionda Lagoon	20 organochlorines and organo-phosphate pesticides, PCBs	3	9
1977-present	California Mussel Watch	Point Conception to Imperial Beach	13 elements, 44 organics	92	10
1986-present	NOAA NS&T Mussel Watch	Point Conception to Imperial Beach, 2 islands	17 elements, 24 chlorinated organics, 19 PAHs	16	11

1. Butler, 1973
2. Alexander *et al.*, 1976; Young and Szpila, 1975
3. Chow, Snyder, and Snyder, 1976
4. de Lappe, Risebrough, and Young, 1980
5. Young *et al.*, 1975
6. Dunn and Young, 1976
7. Eganhouse and Young, 1976
8. Goldberg *et al.*, 1983; Farrington *et al.*, 1982
9. Butler, Kennedy, and Schutzmann, 1978
10. Hayes and Phillips, 1986; Hayes and Phillips, 1987; Phillips, 1988
11. NOAA, 1988, Boehm *et al.*, 1987; NOAA, 1989

SURVEYS OF FISH AND OTHER SPECIES

Risebrough (1969) first reported the occurrence of organochlorine compounds in marine fish and macroinvertebrates from sites within the Southern California Bight. Klein and Goldberg (1970) first reported mercury in fish and invertebrate species at about the same time. However, using museum specimens, MacGregor (1974) was able to analyze for DDT and PCBs in mid-water fish collected from the Southern California Bight as early as 1940.

In rapid succession, a suite of synoptic surveys for contaminants in fish and macroinvertebrates were conducted during 1969-70. These include measurements of DDT and PCBs in barred sand bass from southern California and Baja California sites by Valentine (1972; Valentine and Soule, 1973), DDT in sand crabs from 19 sites between Ensenada and San Francisco Bay (including 10 in southern California) by Burnett (1971), a survey of DDT in 10 species of fish and macroinvertebrates from San Diego and Orange County by Munson (1972), and a survey of DDT in livers of California and Baja California fish by Duke and Wilson (1971) and MacGregor (1972).

In 1971, SCCWRP collected Dover sole (*Microstomus pacificus*) from 17 sites along the coastal shelf and at Santa Catalina Island. Livers were analyzed for 10 trace elements (de Goeij and Guinn, 1972a and b; de Goeij *et al.*, 1974) and for DDT and PCBs (SCCWRP, 1973). Yellow crabs were also taken and analyzed for the two organochlorine groups (SCCWRP, 1973; Heesen and McDermott, 1974).

In 1972, as part of a nationwide program, Butler and Schutzmann (1978) began a 4-year analysis of organochlorines in whole juvenile estuarine fish from three southern California sites including Los Angeles Harbor, Long Beach Harbor, and Mission Bay. Species collected included California halibut (*Paralichthys californicus*), queenfish (*Seriphus politus*), white croaker, walleye surfperch (*Hyperosopon argenteum*), northern anchovy, and Pacific halibut (*Hippoglossus stenolepis*; probably misidentified).

During the early 1970s, two local agencies began annual or more frequent monitoring of organochlorines and some metals in fish and macroinvertebrates. At Palos Verdes, the County Sanitation Districts in 1971, began monitoring for organochlorine compounds and mercury in Dover sole, black perch (*Embiotoca jacksoni*), and kelp bass. Sampling continued approximately semiannually until 1977 (Smokler *et al.*, 1979); with re-surveys in 1980, 1983, and 1985 (CSDLAC, unpublished data) Off Huntington Beach, the CSDOC began monitoring various species of bottomfish, macroinvertebrates, and water-column fish in 1974. Since then sampling has been conducted at least annually through 1986. Together, these two monitoring efforts have produced contaminant measurements for over 2,000 samples of fish and macroinvertebrates representing at least 40 species. Imbedded in these data are species-specific time series, such as reported by Smokler *et al.* (1979) and Young, Gossett, and Heesen (1988).

During 1975-77, SCCWRP conducted a detailed set of sampling activities to document geographical trends in metal, pesticide, and PCB contamination of 12 popular seafood fish and invertebrate from coastal and island sites between Port Hueneme and San Diego (Young *et al.*, 1978; Young *et al.*, 1981a). Concurrently, NOAA NMFS sampled 12 species of fish and invertebrates from the Bight for trace elements (Hall *et al.*, 1978).

Flatfish collected in seven regions during the 1977 SCCWRP 60-m survey (Word and Mearns, 1979) were analyzed for organochlorine compounds in muscle and liver but the data have not been published. Also in 1977, 36 samples of Dover sole tissues from Palos Verdes and a reference site at Dana Point were analyzed for trace elements and organochlorine compounds as part of a three-area nationwide comparison study (Sherwood, 1982).

In 1978, SCCWRP launched the first of several studies to examine the biomagnification of organochlorine compounds, trace elements, and other chemicals in various marine ecosystems of the Southern California Bight. Seventeen species of coastal pelagic organisms were sampled in 1978 (Young *et al.*, 1980) and 1980 (Schafer *et al.*, 1982). Newport Bay was also sampled once in 1978 and twice in 1980 (MBC and SCCWRP, 1980). Palos Verdes was sampled in 1980-81 (Schafer *et al.*, 1982), and Los Angeles Harbor in 1979 (Mearns and Young, 1980). Concurrently, as part of a nationwide survey, Gadbois and

Maney (1983) analyzed PCBs in flesh of fin fish collected by the University of Southern California in and outside of Los Angeles Harbor and at Santa Catalina Island. Most of the samples were also measured for arsenic and selenium by Goeders (1982).

During the early 1980s, various investigators sampled fish and macroinvertebrates at scattered points along the coast for various purposes. However, no regionwide surveys were conducted again until the 1985 SCCWRP Reference Survey (Thompson et al., 1987) at 13 of the original sites sampled in 1977 by Word and Mearns (1979).

In 1980-81, a second synoptic "seafood" survey was conducted to determine concentrations of DDT, PCBs, and B(a)P in 12 sport fish species from 13 sites along the Los Angeles County coast between Point Dume and Dana Point (Gossett et al., 1982; 1983b). White croaker were sampled at all sites and at least two other species at five of the sites. In addition, a scan was performed to determine concentrations of all 132 EPA Priority Pollutants in samples of white croaker from five of the sites.

The 1980-81 seafood survey and the 1980 coastal pelagic surveys by SCCWRP were the only regionwide surveys of contaminants in fish and macroinvertebrates during the early 1980s.

In 1985, a third, large-scale survey of fish was conducted by staff of the LARWQCB. Kelp bass and black perch were collected from Palos Verdes, Santa Catalina Island, and Santa Barbara Island and analyzed for organochlorine compounds by Risebrough (1987). Fish and sediment from the San Pedro Basin and white croaker from local piers were also analyzed.

In 1984, the NMFS initiated sampling of liver tissue of four species of nearshore fish at several NOAA Benthic Surveillance Project sites including sites in Santa Monica Bay, near San Pedro in Los Angeles Harbor, near the Long Beach-Seal Beach boundary, Dana Point, San Diego Bay (outside the harbor), and San Diego Harbor (Malins et al., 1986). Additional samples were taken at other sites (Malins et al., 1987). NS&T sampling was conducted annually during the summer. In 1985, the San Pedro Basin site off Palos Verdes was dropped and replaced by an adjacent San Pedro site inside the west breakwater. Other adjustments and additions were made in 1986.

During 1976-78, under BLM sponsorship, a variety of investigators sampled fish, benthic macroinvertebrates, and intertidal invertebrates at many sites throughout the Bight for metals and petroleum hydrocarbons. It has been difficult to account for all the samples and survey events and these data are not reviewed here.

There have been many additional surveys of contaminants in fish and macroinvertebrates from individual sites and monitoring areas. These data have been acquired but, with a few exceptions, they have not been included in this review. Instead it was decided to portray the geographic and taxonomic breadth of contamination of fish and shellfish by focusing on several large data sets from one laboratory--SCCWRP. These data (Table 3.3) include results from the 1975-77 seafood survey (Young et al., 1978), a suite of surveys offshore and harbor surveys to document pollutant flow through marine food webs (Young et al., 1981a and b; Schafer et al., 1982; MBC and SCCWRP, 1980), the 1981 seafood survey (Gossett et al., 1983b), the 1977 60-m survey (SCCWRP, unpublished data), the 1985 Reference Survey (Thompson et al., 1987), and the 1976-77 survey of three coastal areas (Sherwood, 1982). These data were amended with information from the 1985 LARWQCB PCB and pesticide surveys (Risebrough, 1987). Finally, trends were portrayed using published (Smokler et al., 1979) and unpublished data largely from the CSDLAC.

Table 3.3. Principal regionwide or taxonomically diverse surveys of contaminants in fish and macroinvertebrates of the Southern California Bight, 1971 through 1985.

Year	Name of Survey	Areas Surveyed	Organisms	Tissue	Analytes	Sites	References
1970-71	DDT in Sand Crabs	Gaviota to Ensenada	Sand Crab	whole	DDT	10	1
1971-72	Dover Sole Survey and Santa Catalina Island	Port Hueneme to Dana Point Dover sole		muscle	PCBs, DDT	24	2
1971-72	Dover Sole Survey and Santa Catalina Island	Port Hueneme to Dana Point Dover sole	liver	12 metals	3	3	
1972-76	NPMP--Estuarine Fish harbors, Mission Bay	Los Angeles-Long Beach 9 fish species	whole	PCBs, DDT	3	4	
1975-77	Contaminants in Seafood Organisms	Oxnard to San Diego, 2 islands, and Cortez Bank	9 shellfish species and 9 fish species	edible tissues	28 elements, PCB, and DDT	10	5
1977	60-Meter Survey	Gaviota to San Diego sole, Pacific sanddab	Dover sole, English sole	muscle and liver	PCBs, DDT	7	6
1978	Newport Bay Survey	Upper Newport Bay	algae and 5 fish species	muscle and DDT	12 metals, PCBs, 3	10	
1978	Newport Bay Survey	Upper Newport Bay	algae, 5 fish species, a	muscle	Hg, PCBs, and DDT	3	11
1978-79	Coastal Pelagic Ecosystem Survey	San Pedro Channel	9 fish species and sharks nd crab	muscle	HG		7
1979	Harbor Ecosystem Survey	Los Angeles Harbor	kelp, clam, and 3 fish species	muscle PCBs, and DDT	13 metals, B(a)p, 1	8	
1980	Coastal Pelagic Ecosystem Survey	Open coastal waters	zooplankton, squid, 8 fish species, and 3 sharks	muscle	10 metals, PCBs, and DDT		9
1980	NOAA Microconstituents Survey (PCB)	Los Angeles Harbor, Santa Catalina Island	8 fish species and horseshoe kelp	muscle	PCBs	4	13

Table 3.3.   (continued)

Year	Name of Survey	Areas Surveyed	Organisms	Tissue	Analytes	Sites	References
1980-81	Palos Verdes Benthic Ecosystem	Palos Verdes Shelf	mysids, prawn, 3 fishspecies, and spiny dogfish	muscle	8 metals, PCBs, and DDT	2	12
1980-81	Pier Seafood Survey Los Angeles-Long Beach harbors	Malibu to Dana Point,	16 fish species	muscle	B(a)p, PCBs, DDT non-purgeable EPA Priority Pollutants	16	14
1984	NMFS Marine Pollution Study Los Angeles	Santa Monica Bay to Dana Point	white croaker	liver, stomach contents	18 PAHs, PCBs, 14 pesticides	6	15
1984-present	NOAA NS&T Benthic Surveillance	Santa Monica Bay to San Diego Harbor	5 fish species	liver	17 metals, 18 PAHs PCBs, 14 pesticides	6	16
1985	Organic Contaminants in Los Angeles Area	Channel Islands to Los Angeles Harbor, Long Beach, San Pedro Basin Gaviota to U.S.-Mexico boundary	crab and 5 fish species	muscle liver	PCBs, DDT, and 10 pesticides	12	17
1985	Reference Survey	Gaviota to U.S.-Mexico boundary	prawn and 4 sole and sanddab species	liver	PCBs, DDTs, HCB, and lindane	13	18

1. Burnett, 1971
2. SCCWRP, 1973; Young, McDermott, and Heesen, 1976b
3. de Goeij and Guinn, 1972a, 1972b; de Goeij et al., 1974
4. Butler and Schutzmann, 1978 and original data
5. Young et al., 1978; Young et al., 1981a; Mearns and Young, 1980; Goeders, 1982
6. SCCWRP, unpublished data
7. Mearns and Young, 1980; Goeders, 1982
8. Mearns and Young, 1980; Goeders, 1982
9. Schafer et al., 1982; Goeders, 1982

10. Mearns and Young, 1980; Goeders, 1982; Young, 1988
11. MBC and SCCWRP, 1980; Goeders, 1982
12. Schafer et al., 1982; Goeders, 1982
13. Gadbois and Maney, 1983
14. Gadbois and Maney, 1983
17. Mearns and Young, 1980; Goeders, 1982
15. Malins et al., 1986a; Malins et al., 1987
16. Malins et al., 1986b; NOAA, 1987a and b and unpublished data
17. Risebrough, 1987
18. Thompson et al., 1987

DISTRIBUTION AND ABUNDANCE OF DATA

That portion of the data concerning contaminant levels in mussels and fish and other species was examined to determine distribution in relation to time, geography, species, and tissue types.

Temporal and Geographic

The longest time series of pollutant data for any species was 32 years for DDT in whole northern lampfish (*Stenobrachius leucopsarus*; 1940-71) a small mid-water species. This unusually long series is due to the retrospective sampling for this pesticide in specimens collected since the early 1940s by the CalCOFI Program (MacGregor, 1974).

Samples of marine life that have been analyzed for chlorinated hydrocarbons were collected over the period 1940 through 1985. An initial peak in sampling frequency, which was due almost entirely to retrospective analyses of DDT in mesopelagic fish captured during CalCOFI surveys and analyzed by MacGregor (1974), occurred in 1950-55. A second, larger peak, occurred from 1970-77 with especially high numbers of 374 samples in 1972, 412 in 1974, and 415 in 1975. These high numbers are due largely to surveys conducted by SCCWRP, the CSDLAC (Smokler *et al.*, 1979), and by the CSDOC. A third sampling peak (369 samples) occurred in 1981, due again to surveys largely conducted by SCCWRP. The final most recent peak in 1985 (399 samples), was due in part to a survey by the LARWQCB (Risebrough, 1987).

Sampling effort has been distributed inequitably among various bays, islands, and lagoons within the Bight. The largest number of samples (1527) were from the Palos Verdes Peninsula followed by Orange County (885), the San Pedro Channel (433), Santa Monica Bay (337), and other regions in the Bight not otherwise identified from Figure 3.2 Effort has generally decreased with distance from the Los Angeles County/Orange County area. Fortunately, however, at least some data were discovered for bays, lagoons, harbors, and marinas including Marina del Rey, Los Angeles-Long Beach harbors, Bolsa Bay, Newport Bay, Dana Harbor, San Diego Harbor, and the Tijuana Estuary.

Taxonomic and Tissue Distributions

At least 131 taxa of fish, shellfish, and other invertebrates from the Bight have been analyzed for PCBs and chlorinated pesticides. The most frequently sampled fish groups include flatfish (1,276 samples, 15 species), rockfish (494 samples, 24 species), croaker (406 samples, 5 species), perch (389 samples, 8 species), and bass (369 samples, 6 species). Bivalve mollusks are the most frequently analyzed invertebrates (408 samples, 6 species; Figure 3.3).

The most frequently sampled species include Dover sole, 627 samples; northern lampfish, 352 samples; kelp bass, 300+ samples; black perch (*Embiotoca jacksoni*), 300+ samples; Pacific sanddab (*Citharichthys sordidus*), 103 samples; and white croaker, 87 samples.

Muscle of fish and crustaceans has been the most frequently sampled tissue (1,773 samples), followed by liver (592), whole organisms (442), and whole organisms less shells (347; Figure 3.4). However, other tissues and products have been analyzed including kidney, heart, brain, stomach contents, fat, and fish oil.

Most of the biological samples accounted for in the NOAA Ocean Assessments Division files (3000) have been collected and analyzed by local public agencies, sanitation districts and their consultants or research organizations such as SCCWRP. State agencies have analyzed about 1000 samples and federal agencies about 1000 samples. The balance are from academic and private organizations.

Chemical Diversity

A myriad of chemicals have been analyzed in wastewaters, sediments, and marine life of the Southern California Bight. To gain some insight into what has been found, lists were compiled of organic and inorganic chemicals from six major biological survey activities that were conducted using current analytical methods and that also focused on harbor and wastewater outfall areas where fish and invertebrates are most likely to be exposed to contaminants. These surveys included collections at the Palos Verdes, Santa Monica Bay, and Orange County outfall areas sampled by SCCWRP and sanitation agencies and urban harbor areas occupied by state and NOAA Mussel Watch surveys (Table 3.4).
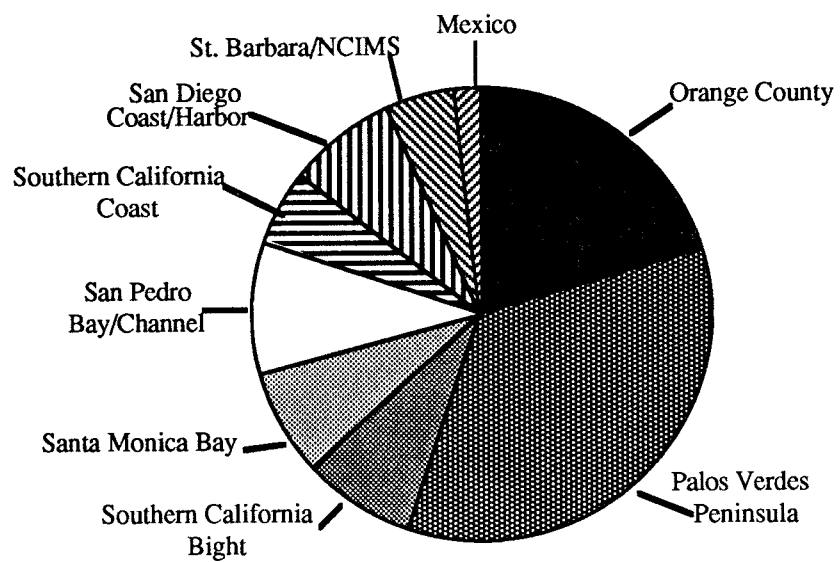
Figure 3.2. Distribution of chlorinated hydrocarbon samples by area.
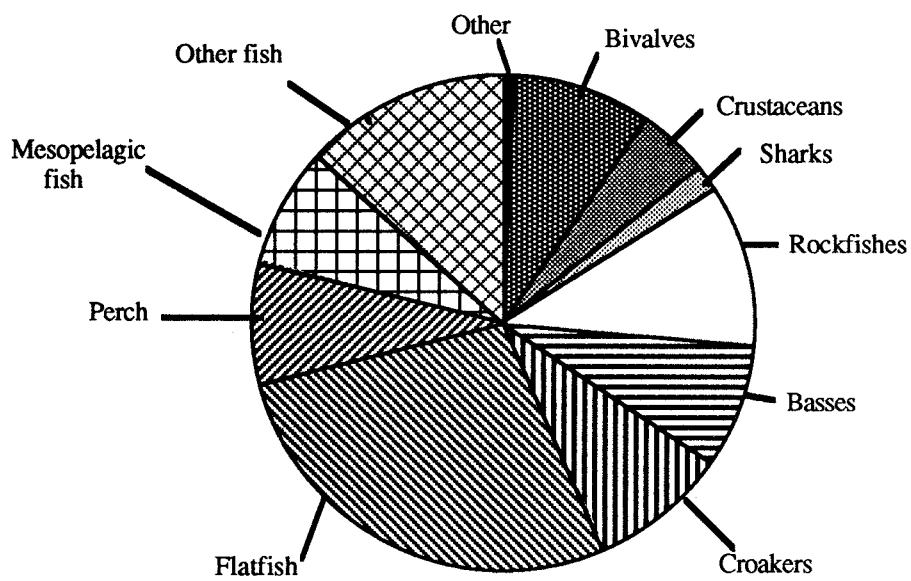
Figure 3.3. Distribution of chlorinated hydrocarbon samples among various taxa.
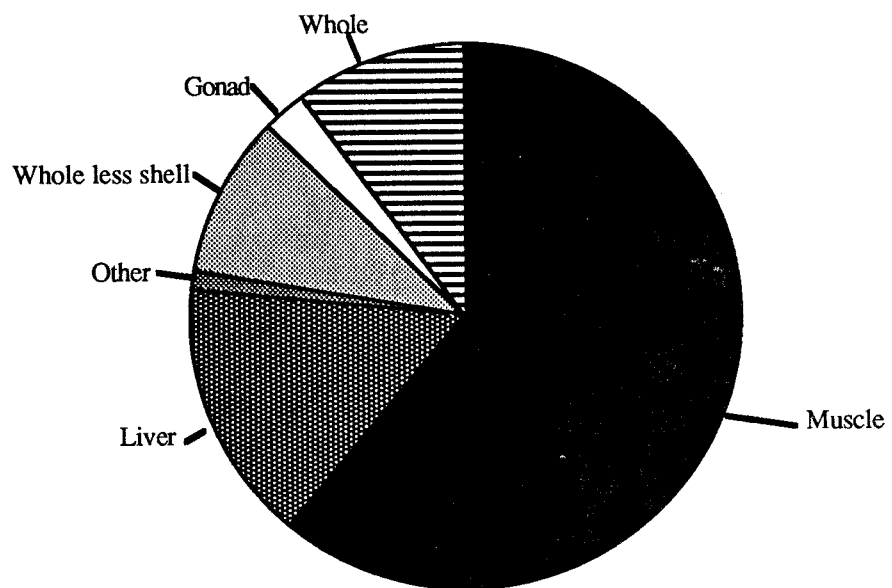
Figure 3.4. Distribution of chlorinated hydrocarbon samples by tissue type.

Table 3.4. List of organic chemicals looked for or found in marine organisms of the Southern California Bight with an indication of their occurrence.

CLASS/COMPOUND	OCCURRENCE	CLASS/COMPOUND	OCCURRENCE
CHLOROBENZENES		**PAHs**	
Chlorobenzene		Acenaphthene	
Dichlorobenzene, 1,2-	X	Acenaphthylene	
Dichlorobenzene, 1,3-		Anthracene	
Dichlorobenzene, 1,4-	X	Benzo(a)anthracene	X
Dichlorobenzene, p-		Benzo(a)fluoranthene	
Trichlorobenzene, 1,2,4-	X	Benzo(a)pyrene	X
Trichlorobenzene, 1,3,5-	X	Benzo(b)fluoranthene	
		Benzo(e)pyrene	X
		Benzo(ghi)perylene	
EXTRACTABLE ORGANICS		Benzo(k)fluoranthene	
		Biphenyl	X
Aniline		Chloronaphthalene, 2-	
Benzidine		Chrysene	X
Benzoic acid		Dibenzo(a,h)anthracene	
Benzyl alcohol		Dimethylnaphthalene, 2,6-	X
Chloroaniline, 4-		Fluoranthene	X
Dichlorobenzidine, 3,3-		Fluorene	X
Dinitrotoluene, 2,3-		Indeno(1,2,3-CD)pyrene	
Dinitrotoluene, 2,6-		Methylnaphthalene, 2-	X
Ether, 2-chloroethylvinyl		Methylphenanthrene, 1-	X
Ether, 4-chlorophenyl		Naphthalene	X
Ether, 4-chlorophenyl phenyl		Perylene	
Ether, bis (2-chloroethyl)		Phenanthrene	X
Ether, bis (2-chloroisopropyl)		Pyrene	X
Hexachlorethane		Trimethylnaphthalene, 2,3,5-	X
Hexachlorobutadiene			
Hexachlorocyclopentadiene		**PCBs**	
Isophorone			
Ketone, methyl ethyl		Arochlor 1016	
Methane, bis (2-chloroethyl)		Arochlor 1221	
		Arochlor 1232	
Nitroaniline, 2-	X	Arochlor 1242	
Nitroaniline, 3-	X	Arochlor 1248	
Nitroaniline, 4-	X	Arochlor 1254	
Nitrobenzene	X	Arochlor 1260	
Nitrosodimethylamine, n-		Polychlorinated biphenyl, 2CL	
Nitrosodiphenylamine, n-		Polychlorinated biphenyl, 3CL	
Nitrosodipropylamine, n-		Polychlorinated biphenyl, 4CL	
Pentanol, 4-methyl-2-		Polychlorinated biphenyl, 5CL	
TCDD		Polychlorinated biphenyl, 6CL	
		Polychlorinated biphenyl, 7CL	
OTHER ORGANICS		Polychlorinated biphenyl, 8CL	
		Polychlorinated biphenyl, 9CL	
Dibenzofuran			
Dimethyldisulfide			

Table 3.4. (continued).

CLASS/COMPOUND	OCCURRENCE	CLASS/COMPOUND	OCCURRENCE
PESTICIDES, CHLORINATED		**PHENOLS**	
Aldrin	X	Chlorophenol, 2-	
Chlordane, trans-		Dichlorophenol, 2,4-	
Chlordane, cis-	X	Dimethylphenol, 2,4-	
Chlordane, trans-	X	Dinitrophenol, 2,4-	
Chlordane, oxy-	X	Methylphenol, 4-chloro-3-	
Chlordene, trans-	X	Methylphenol, 4,6-dinitro-2-	
Chlordene, cis-	X	Nitrophenol, 2-	
Chlordene		Nitrophenol, 4-	
Dacthal (DCPA)	X	Phenol	X
DDD, o,p'- (DDD, 2,4'-)	X	Phenol, 2-methyl	
DDD, p,p'- (DDD, 4,4'-)	X	Phenol, 4-methyl	X
DDE, o,p'- (DDE, 2,4'-)	X	Tetrachlorophenol	X
DDE, p,p'- (DDE, 4,4'-)	X	Tetrachlorophenol, 2,3,5,6-	X
DDT,o,p' - (DDT, 2,4'-)		Trichlorophenol, 2,4,5-	X
DDT,p,p' - (DDT, 4,4'-)		Trichlorophenol, 2,4,6-	
DDMS, p,p'-			
Dieldrin	X		
Endosulfan I	X		
Endosulfan II	X	**VOLATILE ORGANICS**	
Endosulfan sulfate	X		
Endrin	X	Acetone	
Endrin aldehyde		Acrolein	
HCH (BHC) unspecified	X	Acrylonitrile	
HCH (BHC) alpha		Benzene	
HCH (BHC) beta		Bromodichloromethane, DCBM-	
HCH (BHC) delta		Bromoform	
HCH (BHC) gamma (lindane)	X	Carbon disulfide	
Hexachlorobenzene	X	Carbon tetrachloride	
Heptachlor	X	Chlorobenzene	
Methoxychlor	X	Chloroform	
Mirex	X	Dibromochloromethane, DBCM	
Nonachlor, trans		Dichlorethane, 1,1-	
Pentachlorophenol	X	Dichlorethane, 1,2-	
Toxaphene	X	Dichloropropane	
		Dichloropropane, 1,2-	
PESTICIDES, OTHER		Dichloropropane, 1,3-	
		Ether, 1,2-Dichloro	
Bromoform		Ethyl chloride	
Chlorbenside	X	Ethylbenzene	X
Chlorpyrifos		Ethylene chloride	
Diazinon		Hexanone, 2-	
Parathion, methyl		Ketone, methyl isobutyl	
Tetradifon			

Table 3.4. (continued).

CLASS/COMPOUND	OCCURRENCE	CLASS/COMPOUND	OCCURRENCE
VOLATILE ORGANICS (Continued)		**TRACE ELEMENTS**	
Methyl bromide		Aluminum	X
Methyl chloride		Antimony	X
Methyl ethyl ketone		Berylium	X
Methylene chloride		Cadmium	X
Perchloroethylene		Copper	X
Styrene		Iron	X
Tetrachloroethane, 1,1,2,2-		Lead	X
Tetrachloroethylene	X	Manganese	X
Toluene	X	Mercury	X
Trichloroethane, 1,1,1-	X	Nickel	X
Trichloroethane, 1,1,2		Selenium	X
Trichloroethylene		Silicon	X
Vinyl acetate		Silver	X
Vinyl chloride		Thalium	
Xylene isomer		Tin	X
Xylenes		Titanium	X
		Zinc	X

PHTHALATES

Phthalate, bis (2-ethylhexyl)
Phthalate, butyl benzyl
Phthalate, di-n-butyl
Phthalate, diethyl
Phthalate, dimethyl
Phthalate, di-n-octyl

Data sources:

CSDLAC, unpublished
CSDOC, unpublished
Philips, 1988
NOAA, 1988
Gosset, Brown, and Young, 1983a
Young and Heesen, 1978

Of a cumulative list of 170 extractable and volatile chemicals searched for in these surveys, 62 were found at or above prevailing analytical detection limits (Table 3.4 and summary in Table 3.5). These included 28 of 36 chlorinated pesticides, 12 of 26 PAHs, 4 of 7 PCB Aroclor mixtures, 4 of 8 chlorinated benzenes, 4 of 15 chlorophenols, 6 of 43 volatile organics and cleaning solvents, 1 of 6 additional pesticides, and none of 29 other extractable compounds.

Table 3.5. Summary of cumulative list of organic compounds searched for or found in six survey efforts.

GROUP	NUMBER SEARCHED FOR	NUMBER FOUND
Chlorinated pesticides	36	28
PAHs	26	12
Chlorinated benzenes	8	4
Phenols	15	4
Volatile organics	42	6
Extractable organics	30	0
Other pesticides	6	1
PCBs by aroclors	7	4
PCBs by chlorination number	8	7
Total (w/aroclors)	170	62
Total (w/chlorination)	171	65

In addition, Gosset *et al.* (1982) submitted samples of muscle of white croaker from five 1981 collection sites (Santa Monica Bay outfall, Palos Verdes, Cabrillo Pier and Belmont Pier in Los Angeles Harbor, and southern Orange County) to California Analytical Laboratories for analysis of 57 extractable (non-purgeable) organic compounds on the EPA Priority Pollutant List. None of 46 base neutral compounds were detected but phenol was present above the GC/MS detection limit of 25 parts per billion (ppb) ww. Phenol concentrations ranged from 42 ppb ww in fish from Palos Verdes (Whites Point) to 231 ppb ww in fish from a southern Orange County "control" or "reference" site. Dioxin was also looked for but not found. Of 26 trace elements searched for, 25 have been quantified in one or more substrates (Table 3.4). In addition to those covered in subsequent chapters of this report (Ag, As, Cd, Cr, Cu, Hg, Pb, Se, Sn, and Zn), levels have been quantified in mussels from coastal and island sites for B, Ba, Co, Mg, Mn, Mo, Ni, Si, Sr, W, and V (SCCWRP, 1973).

It is likely many more compounds occur in sediments and in waste streams near the areas where marine organisms were collected, but those data were not examined. Gossett *et al.* (1984) and Eganhouse and Kaplan (1981), Eganhouse *et al.* (1981), and Eganhouse *et al.* (1985) list hundreds of organic contaminants entering coastal waters via sewage and river runoff. Nonetheless, with current techniques, it appears that pesticides, PAHs, and a few phenols, benzenes, and phthaltes dominate the diversity of parent compounds of organic contaminants in southern California marine organisms whereas many other volatile and extractable organic compounds are not accumulated.

Most of the encountered chemicals occurred infrequently. For example, of 17 sites sampled as part of the NOAA Mussel Watch Project, the maximum number of PAHs found at any one site was 7 out of 18 PAHs; 6 PAH compounds occurred at an additional site, three at 2 sites, two at 4 sites, one at 3 sites, and none at 4 sites. Likewise for pesticides, one or more DDT metabolites have been found in all fish and invertebrates sampled and chlordane and dieldrin in some. The remaining 25 pesticides have only been found in a few samples at a few sites.

Thus, despite the potential variety of possible compounds of concern and probable environmental occurrence, relatively few are known to occur in marine organisms of the Southern California Bight at frequencies sufficient to determine spatial and temporal patterns.

The following chapters explore what is known about the geographic, temporal, and taxonomic distribution of the most frequently quantified chemicals including 10 trace elements (Ag, As, Cd, Cr, Cu, Hg, Pb, Se, and Zn) and five groups of organic chemicals (DDT, PCBs, chlordane, dieldrin, and PAHs).

SUMMARY AND CONCLUSION

In summary, there is a considerable history of contaminant monitoring and surveys in the Southern California Bight, but there have been very few surveys that have been repeated with sufficient frequency or sampling control to generate time-series data. As a consequence, the history of contamination of sediments, bivalves, fish, and macroinvertebrates in the Bight must be carefully reconstructed on a pollutant-by-pollutant, survey-by-survey basis. The remaining chapters of this report are based on reviews of the most synoptic of the surveys discussed here. A consequence of this selection is that thousands of samples from many dozens of surveys remain to be examined and reviewed.

CHAPTER 4

ARSENIC

Arsenic is a common semi-volatile trace element. The toxic effects of arsenic have been well known for many centuries and have been employed in such products as insecticides and herbicides. However, the environmental chemistry of arsenic is complex, and some forms of the element are less harmful than others. Arsenic has been identified as a carcinogen and has been linked to reproductive disorders (Goyer, 1986).

Arsenic compounds occur naturally in seawater. Potentially significant amounts are also of human origin. These include residues deriving from manufacture and application of arsenic-based pesticides, herbicides, and wood preservatives; waste products from smelting operations; and by-products of the burning of coal. Because natural arsenic is abundant, human inputs are likely to be more important on local, as opposed to global, scales (Menzer and Nelson, 1986).

Arsenic compounds may be trivalent or pentavalent; it is principally the trivalent forms that are toxic, affecting cellular enzyme activity and respiration. Riedel et al. (1987) found that pentavalent arsenic added to anoxic test sediments was rapidly reduced to the trivalent form. They also determined that bioturbation by benthic-dwelling organisms significantly increased the rate of arsenic flux from sediments to water. This would imply that such processes may be important in cycling existing reservoirs of contaminants back into ecosystems, despite reduction or elimination of new (anthropogenic) inputs. Dissolved arsenic can occur in natural waters in both inorganic and organic forms. Organisms isolate and detoxify arsenic by producing organic forms of arsenic. Organic forms of arsenic are thought to be less toxic and more readily excreted than inorganic forms (Friberg, 1988).

A natural arsenic source to southern California coastal waters may be from hydrothermal springs: Punta Bunda submarine hot spring water contained 420,500 µg/L (ppb) compared to 3 ppb in average seawater (Vidal et al., 1978) and 3 to 13 ppb in sewage effluents (Schafer, 1982). In addition, Vidal et al. (1978) noted that rocks from the area "...reveal a very strong sulfurous odor accompanied by a minor sweet garlic-like smell attributable to As or arsenous sulfides." These rocks contained concretions bearing 5 million ppb of arsenic.

There are very few data with which to determine trends in arsenic input into the Southern California Bight. Total emissions from major sewage discharges have been variable, ranging from a low of 8.7 metric tons (mt) in 1982, to 20.9 mt in 1974 (SCCWRP, 1988). No net long-term trend is apparent (Figure 4.1). The 1985 total sewage emission was 15.8 mt (SCCWRP 1987a). Arsenic has not been included in studies of runoff or industrial discharges (SCCWRP, 1973 and 1978; Schafer and Gossett, 1988) or aerial and fire fallout (Young and Jan, 1977), so there is no way to determine the relative significance of the waste water inputs.
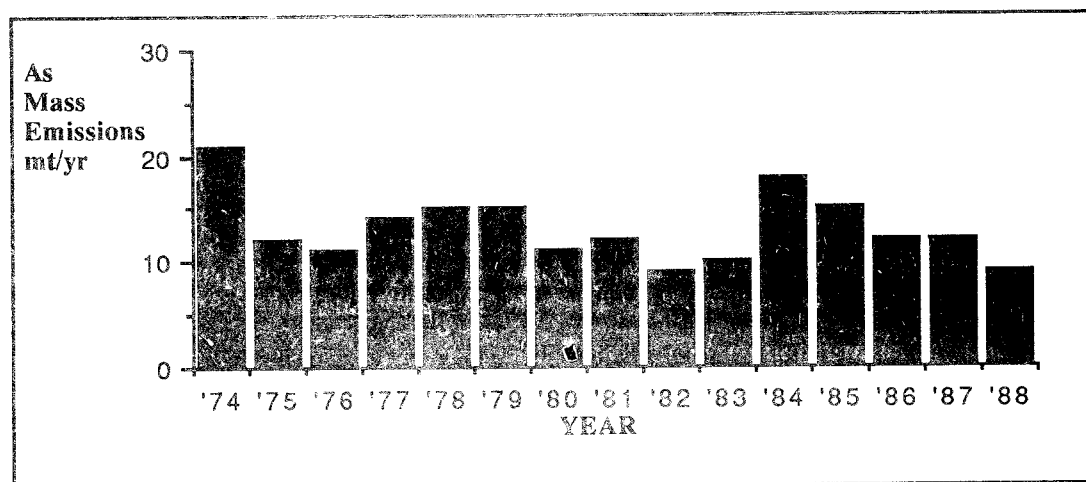
Figure 4.1. Combined annual mass emissions of arsenic for seven southern California wastewater dischargers, 1974-88. Source: SCCWRP, 1989.

ARSENIC IN SEDIMENTS

Measured arsenic concentrations in sediments from one survey of the world's oceans range from 0.04 to 45.5 ppm dw with a mean of 33.7 (Eisler, 1988a). In southern California, the range for all data used in this report was 0.8 to 538 ppm dw. The overall median in recent surveys was 10 ppm dw (Table 4.1).

Arsenic has been measured in comparatively few southern California sediment surveys (Table 4.1). It was included in a few samples from 1970-71 surveys of metals around the five major outfalls (Galloway, 1972 a and b; SCCWRP, 1973) and in 1971 and 1973 surveys at Palos Verdes (Young, 1974). Considerably more data exist for sediments in harbors. Arsenic was measured in Los Angeles-Long Beach harbors in 1973 (Chen and Lu, 1974), 1978 (Soule and Oguri, 1980a) and 1985 (Marine Bioassay Laboratories (MBL), 1986). Several surveys analyzed arsenic in sediments from Newport Bay in 1971 (Young et al., 1975) and in 1980 (MBC and SCCWRP, 1980); from regularly monitored sites in Huntington Harbor, Newport Bay, and Dana Harbor (OCEMA, 1986); from Newport Bay shipyards in 1972, 1981, and 1986 (Liu and Schneider, 1988). San Diego Harbor was sampled in 1971 (Young et al., 1975) and 1983 (Ladd et al., 1983). Also, data now exist for arsenic in sediments from the 15 NOAA NS&T Mussel Watch sites sampled since 1986 and from 5 NOAA NS&T Benthic Surveillance sites sampled since 1984.

Not including data from NOAA NS&T surveys (Table 4.1), arsenic concentrations ranged from 0.8 ppm dw in a sample collected from a site in Upper Newport Bay in 1971 (as cited in Young et al., 1975) to 538 ppm dw in a sample collected from a site along the Palos Verdes shelf in 1974 (Stull and Baird, 1985). In addition to the high concentrations along the Palos Verdes shelf between 1971 and 1985, there is some evidence that harbor sediments also contained elevated levels of arsenic. For example, the median arsenic concentration in Los Angeles-Long Beach harbors was 57 ppm dw in 1978 (but the same sites in 1973 had a median of only 7.8 ppm dw). In contrast, median concentrations in Marina del Rey ranged from 1.0 ppm dw to 14 ppm dw during the period 1977-87, with lower concentrations in the later years (Table 4.1). A pattern related to boat yards or other sources of industrial contamination may have existed in Huntington Harbor, Newport Bay, and Dana Harbor. The median concentration at two sites within Huntington Harbor sampled three times each between November 1983 and November 1984 was 10 ppm dw (range 2 to 21 ppm dw; OCEMA, 1986). The median arsenic concentration in undeveloped Upper Newport Bay in 1971 was 3.5 ppm dw with a range of 0.8 to 3.9, while the median for the more urbanized lower bay was also 3.5 ppm dw, with concentrations ranging up to 10.0 ppm dw (Young et al., 1975). In a more focused study, Liu and Schneider (1988) reported median concentrations in sediments near the Newport Bay shipyards to be 12.5 ppm (range 4.0 to 25.0) in 1981 and 13.0 ppm (range 11 to 15 ppm dw) in 1986 (Table 4.1). These long-term differences between Upper and Lower Newport bay are supported by additional data from OCEMA (1986). The median concentration at two sites within Dana Harbor (near Dana Point) sampled three times each, November 1983 through November 1984, was 7 ppm dw (range 2 to 19 ppm dw (OCEMA 1986). Concentrations in San Diego Harbor sites in 1974 and 1983 and at sites offshore of central Orange County in 1984-85 were intermediate (Table 4.1).

It is difficult to define normal or background arsenic concentrations for the southern California coastal shelf or for bays and lagoons. Arsenic concentrations in one core profile from the Palos Verdes shelf sampled in 1971 decreased from over 100 ppm dw at the surface to about 8 to 10 ppm dw at a depth of about 30 cm (Young, 1974). This deep concentration was similar to the range of 4.3 to 12.0 ppm dw (mean 7.0 ppm dw) recorded from four sites on the seaward side of Santa Catalina Island remote from major urban areas (de Goeij and Guinn, 1972a and b and Table 4.1). Sediments from most shelf sites sampled away from urban areas 1984-1987 NOAA NS&T surveys contained about 10 ppm dw arsenic. These observations seem to imply a coastal sediment background arsenic concentration of about 10 ppm dw. Sediments from the most recent surveys in Los Angeles-Long Beach harbors (1978) and for the Palos Verdes shelf (1985) exceeded this apparent background of 10 ppm dw by a factor of about 5. Arsenic concentrations in samples from the few other areas surveyed (Orange County shelf, Newport Bay, San Diego Harbor, and Marina del Rey) were at, near, or below this level. However, repeated measurements in Upper Newport Bay in the range of 1 to 4 ppm dw would support a lower "baseline" for bays and lagoons, resulting in several-fold enhancements in developed harbors such as Huntington Harbor, Lower Newport Bay, Dana Harbor, and San Diego Harbor.

While existing but limited data suggest sediment arsenic concentrations were well above regional background values only in two areas (Los Angeles-Long Beach harbors and the Palos Verdes shelf, Table

coastal areas. For example, 3 of 23 NOAA NS&T sediment sites sampled in the Southern California Bight between 1984 and 1987 were among the 20 sites with highest arsenic concentrations (normalized to grain size) in the United States (total 176 sites; NOAA, 1988). The non-normalized overall national average arsenic level in sediment (1984-89) was 8.032 ppm dw (median 7.383 ppm dw).

Table 4.1. Mean, median, minimum, and maximum arsenic concentrations in surface sediment from selected surveys, 1970-85 in ppm dw.

SITE	YEAR	N	Mean	Median	Min	Max	SD	Source
NS&T	1986-87	64	11.2		5.2	19	3.3	1
Outfall Areas:								
Palos Verdes shelf	1971 [a]	5	132	127	100	177	28.3	2
	1974 [c]	9	130	62	23	538	163	3
	1980 [c]	9	57.7	61	29	90	20.2	3
	1985 [c]	9	62.9	49.7	13.7	192	50.3	4
	1988 [c]	7	15.2	13	5.0	23.3	6.5	4
Orange County Shelf	1985 [c]	9	13	14	9.7	17	2.4	5
	1984-85 [d]	154	8.9		1.9	33.5		5
Bays and Harbors								
Marina del Rey	1977	11	13	14	2.7	23	7.3	6
	1978	11	9.6	11	2.8	14	3.5	6
	1984	12	1.0	1.0	<1.0	1.0	0.0	7
	1985	12	2.1	1.0	<1.0	5.8	1.6	8
	1987	13	4.6	4.4	<1.0	7.9	1.7	9
Los Angeles-Long Beach harbors	1973	31	8.6	7.8	2.2	19	4.6	10
	1978	20	60	57	22	121	31	11
Upper Newport Bay	1971	3	2.7	3.5	0.8	3.9	2.7	12
Lower Newport Bay	1971	7	4.6	3.5	2.2	10	2.7	12
Newport shipyards	1981	10	13.11	12.5	4.0	25	6.7	13
	1986	6	13.0	13.0	11.0	15	1.4	13
San Diego Harbor	1974	11	7.7	7.9	3.1	21	5.1	14
	1983	20	11		3.9	21		15
Other Areas								
Santa Catalina Island	1971	4	7		4.3	12.0		2
OVERALL					0.8	538		

[a] - cores, 0-10 cm layer   [b] - cores, 24-32 cm layer

[c] - 60-m depths only   [d] - entire grid in all surveys

1. NOAA, OAD, unpublished data
2. deGoeij and Guinn, 1972 a&b; Young, 1974
3. Stull and Baird, 1985
4. CSDLAC, unpublished data
5. CSDOC, unpublished data

6. Soule and Oguri, 1980b
7. Soule and Oguri, 1985
8. Soule and Oguri, 1986
9. Soule and Oguri, 1987
10. Chen and Lu, 1974

11. Soule and Oguri, 1980a
12. Young et al., 1975
13. Liu and Schneider, 198?
14. Young et al., 1975
15. Ladd et al., 1984

In the 1986 NOAA NS&T Mussel Watch and 1984 and 1985 Benthic Surveillance surveys, mean sediment arsenic concentrations ranged from 1.4 ppm dw at a site in San Diego Bay (outside the harbor) sampled in 1984, to 18 ppm dw near the Cabrillo Beach boat ramp in outer Los Angeles Harbor (Figure 4.1). The range for 65 individual samples from 15 sites was 5.2 to 19 ppm dw (mean 11.2, Table 4.1). This is similar to a range of 3.9 to 30 ppm dw for 211 samples from the entire Pacific Coast (NOAA, unpublished data). This range is similar to the historical data. In addition, there were no apparent regional gradients indicative of point sources (Figure 4.2).

In a national review of chemical concentrations in sediment associated with toxic effects, Long and Morgan (1990) calculated values at which toxic effects may first be observed (ER-L) and those that were often associated with toxic effects (ER-M). For arsenic the probable effects range (ER-L to ER-M) is 33-85 ppm dw (Long and Morgan, 1990). Median sediment concentrations have never exceeded the greater of these values. The ER-L value has been exceeded by median sediment concentrations at Palos Verdes and in Los Angeles-Long Beach harbors.

Sediment surveys in 1974 and 1980 (Stull and Baird, 1985) and in 1985 and 1988 (CSDLAC, unpublished data) by the CSDOC along the Palos Verdes shelf indicated that high concentrations measured in the past have declined along the 60-m isobath, from 130 ppm dw in 1974 to 15 ppm in 1988, with intermediate concentrations of 57.7 ppm in 1980 and 62.9 ppm in 1984. The long-term decline and intervening pause in that decline, is commensurate with sewage inputs from the CSDLAC outfall, which declined from 11.3 mt in 1974 to the range of 2.6 to 3.7 mt 1980 to 1983, increasing to 9.6 mt in 1984 and declining again to the range of 4.0 mt in 1986 and 1987 (SCCWRP, 1988). Mean 60-m sediment concentrations now average within a factor of 2 of an apparent background of 6 to 10 ppm dw (Figure 4.3). Lower concentrations were also reported for Marina del Rey during the 1980s than during 1977-78 (Table 4.1), but this could be due to changes in analytical or sampling methods.

ARSENIC IN MUSSELS

Data for concentrations of arsenic in mussels are not numerous for the Southern California Bight. Arsenic was not included in the 1976-78 EPA Mussel Watch (Goldberg *et al.*, 1978) or in any of the SCCWRP mussel surveys of the early 1970s. The CMW Program included only a few measurements for the element at southern California sites. Of the data sets forming the basis for this discussion, only the Mussel Watch Project of the NS&T Program analyzed arsenic in mussel tissue with broad coverage in the southern California region. Values ranged from 6-16 to ppm dw for *M. edulis* and 6.4 to 23 ppm for *M. californianus* These ranges are similar to those previously determined in four separate studies elsewhere in the world (Eisler, 1981) in which concentrations in mussel soft body parts ranged from 1.6 to 16.0 ppm dw.

Arsenic concentrations have varied considerably over short time periods. Concentrations in whole soft tissue (less gonads) of *M. californianus* from six CMW sites sampled in 1982 and 1983 ranged from 6.1 ppm dw at Oceanside to 25.5 ppm dw in one of two collections from Royal Palms near the Whites Point outfall at Palos Verdes. Limited sample sizes and a high degree of variability make interpretation difficult. At the Royal Palms site, arsenic in *M. californianus* varied from 9.6 ppm ww in January 1982 to 25.5 ppm ww in December of the same year. At the Point Loma dolphin tanks, concentrations varied from 8.6 ppm ww in January 1982 to 38.9 ppm ww in January 1983. Records of arsenic mass emissions from nearby municipal treatment plants compiled by SCCWRP do not provide a ready explanation for these results. Arsenic discharges from the Joint Water Pollution Control Plant (JWPCP) outfall, located offshore from Royal Palms, increased 32 percent from 1981 to 1982, but declined 17 percent at the Point Loma plant (Schafer, 1982; Schafer, 1984).
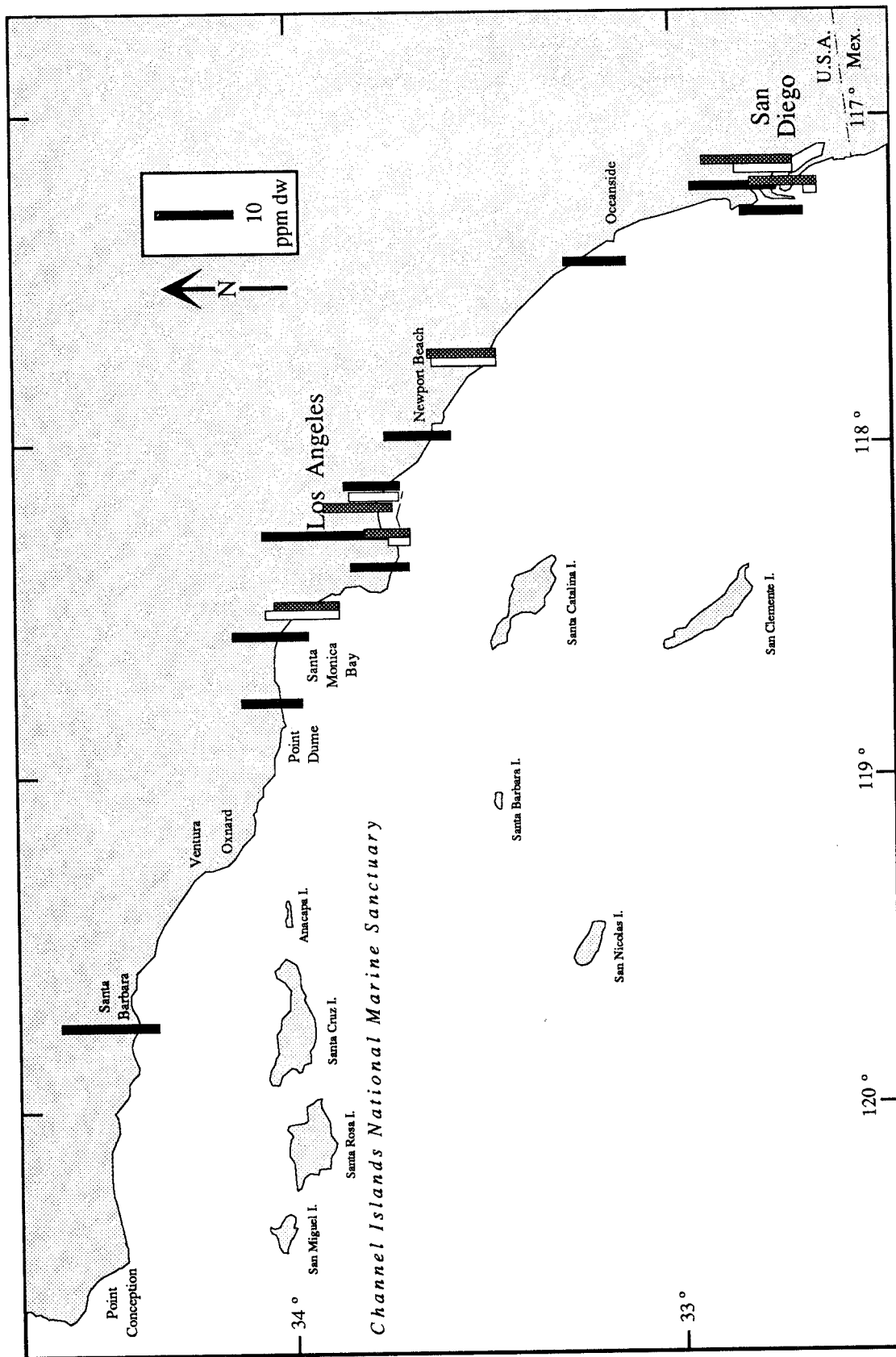
Figure 4.2. Arsenic concentrations in the surficial sediments of the Southern California Bight based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 (▯ and 1985 (▨) and Mussel Watch Project for 1986 (▮) (NOAA, 1988 and NOAA, unpublished data).
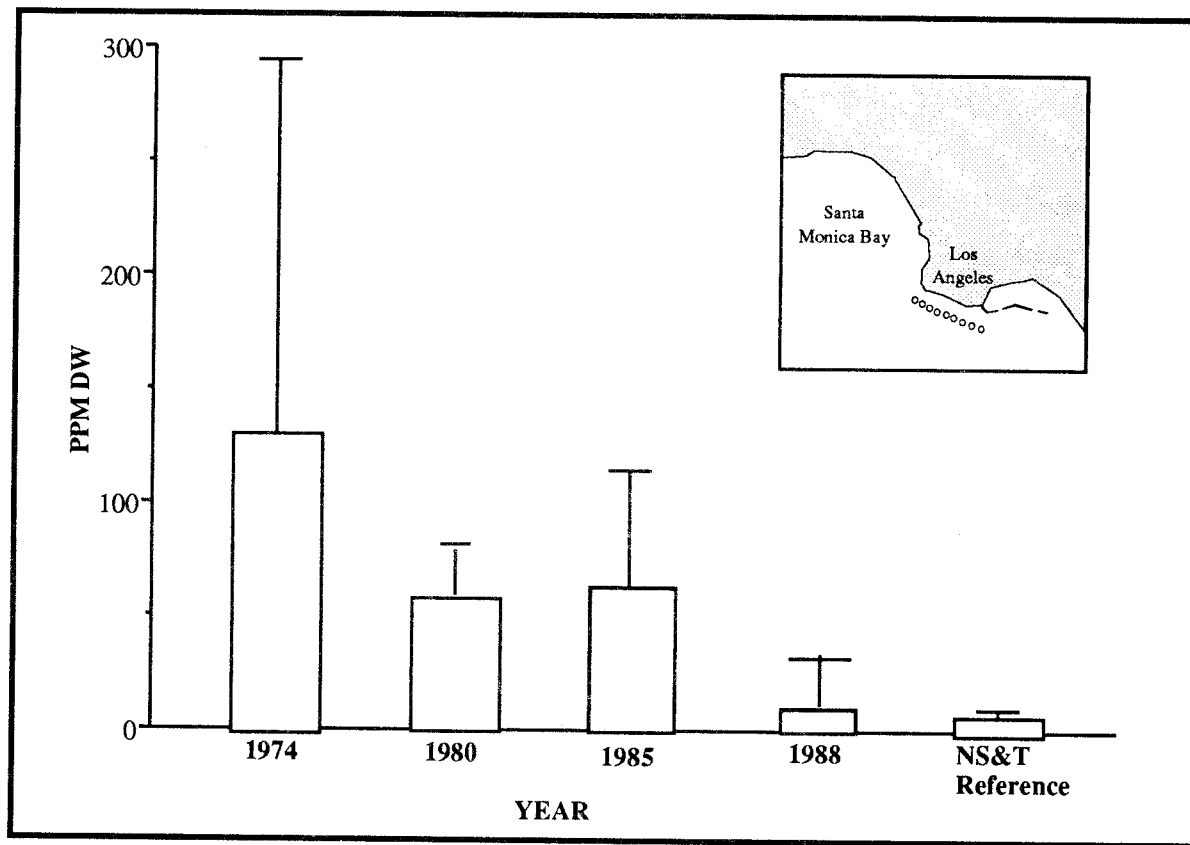
Figure 4.3. Mean arsenic concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC. The reference value is based on the mean of four relatively isolated NOAA NS&T Program sites in the Southern California Bight sampled between 1984 and 1986 (NOAA, 1988 and unpublished data). Inset shows approximate locations of sites sampled by CSDLAC.

Although data for arsenic in the Southern California Bight are limited, one general observation based on NS&T data concerns the locations of the sites yielding the highest concentrations in $M.$ $californianus.$ Locations producing the highest concentrations of arsenic were generally non-urban or rural areas. Those sites were Point Loma (21.7 ppm dw), Santa Cruz Island (19.7 ppm dw), Point Conception (21.3 ppm dw), Santa Catalina Island (16.0 ppm dw), Point Santa Barbara (17.0 ppm dw), and Point La Jolla (14.7 ppm dw; Figure 4.4). Specimens collected at Point Dume and near Anaheim and Newport had the lowest concentrations (10.9, 7.4 and 8.3 ppm dw, respectively).

The highest arsenic concentration in $M.$ $edulis$ was 16.0 ppm dw in San Diego Harbor. Low concentrations in $M.$ $edulis$ occurred at Marina del Rey (10.0) and on the breakwater in San Pedro Bay (7.6). Taken as a whole, the NS&T data suggest no large-scale, regionwide gradient of higher arsenic concentrations with proximity to the Los Angeles area (Figure 4.4).

Placing 1986 southern California NS&T results found nationwide for arsenic in mussel tissue into a broader context, the seven highest arsenic values in mussels from the 1986 NOAA NS&T Program were found in samples from southern California (NOAA, 1988). The overall average level of arsenic in mussels from 1986-89 sampling was similar to levels found at many southern California sites, however. For $M.$ $edulis$, the mean arsenic level nationwide was 8.825 ppm dw (median 8.467 ppm dw). Mean and median levels were higher in $M.$ $Californianus$, however (mean, 14.68 ppm dw; median, 13.333 ppm dw).
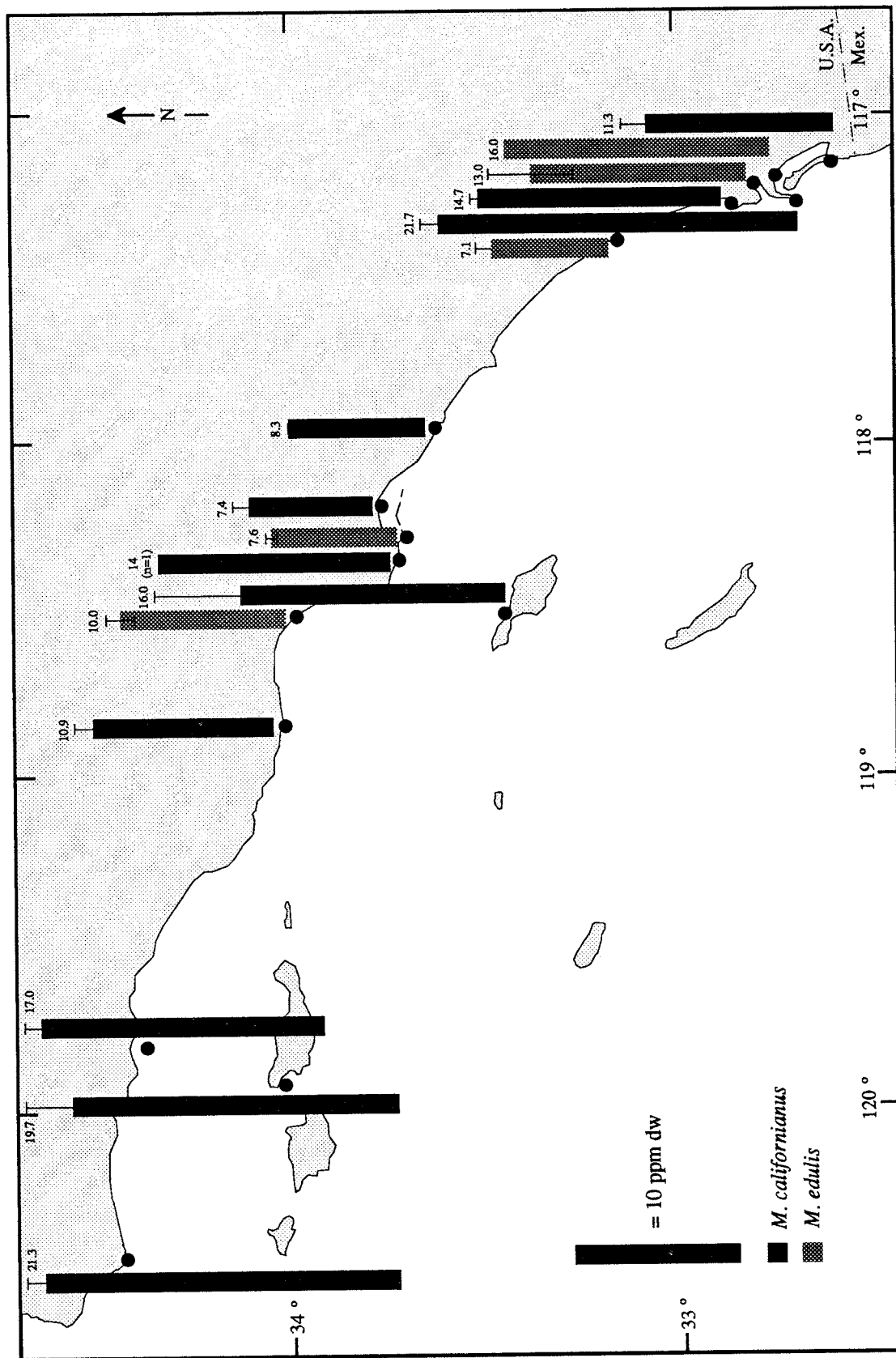
Figure 4.4. Arsenic in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

Arsenic has not been included in bivalve surveys in Baja California (Gutierrez-Galindo *et al.* 1984), so it is not possible to judge trends to the south. Very little information has been collected to determine trends in arsenic levels in mussels over time. NOAA's NS&T Program found that arsenic in mussels increased at two sites between 1986 and 1988. Increases were greater at Newport Bay than at La Jolla (NOAA, 1989)

ARSENIC IN FISH AND OTHER SPECIES

Arsenic has been measured in at least 341 samples of 40 species of marine organisms from the Bight, including 21 species of fish, 2 of sharks, 3 of echinoderms, 4 of crustaceans, and 5 of mollusks. The principal data sets examined included a 1971-72 survey of livers of Dover sole (17 sites, 39 samples; de Goeij *et al.*, 1974); surveys of edible tissues of seafood organisms collected from several bay, harbor, and coastal ecosystems between 1975 and 1980 (Goeders, 1982); the 1984 NOAA Benthic Surveillance data (NOAA, 1987a and b); a pre-1974 survey of Dover sole and crab by Fowler *et al.* (1975); and data from 1984-85 monitoring surveys off Huntington Beach by the CSDOC (1985).

Concentrations of arsenic in muscle and other edible tissues ranged from 0.08 ppm ww in a composite of striped bass from Newport Bay in 1978 (Goeders, 1982) to 60.1 ppm ww in a composite of the muscle of yellow crab (*Cancer anthonyi*) collected at Palos Verdes in 1976 (Table 4.2). In general, arsenic concentrations were much higher in muscle of invertebrates especially abalone (*Haliotis crachcrodii*), lobster (*Panulirus interruptus*), and yellow crab than in fish, leading Goeders (1982) to conclude that arsenic does not undergo biomagnification in marine ecosystems of the Bight.

Muscle tissue of one fish species (Pacific sanddab) and two sharks (mako [*Isurus oxyrinchus*] and white [*Carcharodon carcharias*]) contained considerably more arsenic than other vertebrates. Mean concentrations in muscle composites of Pacific sanddab from two sites were 5.7 ppm ww at Palos Verdes and 10.4 ppm ww at Santa Catalina Island. Arsenic in muscle of sharks ranged from 2.5 to 4.7 ppm ww (Goeders, 1982; Schafer *et al.*, 1982; Table 4.2).

Arsenic was examined in popular seafood organisms in three studies. The most extensive was a 1975-77 collection of nine popular seafood species from six coastal and island sites collected as part of a regional seafood collection (Young *et al.*, 1978) subsequently analyzed for arsenic by Goeders (1982). These data show that in six of nine species (black abalone, purple-hinge scallop [*Hinnites multirugosus*], California spiny lobster, Pacific sanddab, California halibut, and kelp bass), arsenic was no higher in collections from one or more distant reference sites than at Palos Verdes (Whites Point) discharge area, which harbored elevated sediment concentrations (Table 4.2 and Young *et al.*, 1978). In fact, concentrations were considerably lower at Palos Verdes than at "reference" sites for three species: black abalone, Pacific sanddab, and California halibut (Table 4.2 and Young *et al.*, 1978). Conversely, mean arsenic concentrations were higher at Palos Verdes than at other sites for three species: gonads of red sea urchin (*Strongylocentrotus franciscanus*), muscle of yellow crab, and possibly, muscle of bocaccio (*Sebastes paucispinis*) (Table 4.2). However, Fowler *et al.* (1975) reported lower muscle arsenic concentrations in yellow crab from Palos Verdes than from a site off Santa Barbara, but found the opposite situation for Dover sole muscle (Table 4.2).

Arsenic was measured in 154 samples of sediments and in replicate tissue composites of 10 species of fish and invertebrates during 1985-86 sampling around the Orange County outfalls (5 to 10 km offshore of Huntington Beach) during the 1985-86 monitoring season (CSDOC, 1987). Muscle concentrations were lowest in barred sandbass (median 0.22 ppm ww), California tonguefish [*Symphurus atricauda*] (0.37 ppm ww), white croaker (0.48 ppm ww), and Pacific mackerel (0.48 ppm ww); intermediate in speckled sanddab [*Citharichthys stigmaeus*] (0.76 ppm ww); and highest in ridgeback pawn [*Sicyonia ingentis*] (0.9 ppm ww) and hornyhead turbot (1.4 ppm ww). In contrast, median concentrations were much higher in soft parts of other benthic invertebrates, ranging from 3.5 ppm ww in pyloric crease of the seastar, *Pisaster brevispinus,* to 4.7 ppm ww in whole soft tissue of clams (*Tellina*). These animals were collected over sediments containing an average of 8.9 ppm dw of arsenic (range 1.92 to 33.5 ppm dw).

Sampling was only sufficient with prawns to determine spatial gradients. In this case, arsenic in muscle tissue was at least twice as high in animals from the reference site (1.4 or 1.6 ppm ww) as in animals collected near the outfall diffuser (0.26 and 0.69 ppm ww).

Table 4.2. Arsenic (ppm ww) in marine organisms from the Southern California Bight.

Common Name	Site	Year	No. of Samples	Mean	Median	Minimun	Maximun	Standard Deviation	Source
Kelp (internal stipe)	Los Angeles Harbor	1979	5	5.32	5.60	3.55	6.40	1.06	Goeders, 1982
Enteromorpha (whole)	Newport Bay	1978	3	1.74	1.65	1.65	1.90	0.14	Goeders, 1982
Green Algae	Newport	1978	1	1.67	-	-	-	-	Goeders, 1982
Zooplankton (whole)	Point Dume	1980	3	1.04	0.91	0.86	1.35	0.27	Goeders, 1982
	Santa Catalina Island	1981	1	1.70	-	-	-	-	Goeders, 1982
	Santa Monica	1981	1	1.76	-	-	-	-	Goeders, 1982
Gaper clam (neck)	Los Angeles Harbor	1979	5	1.25	1.24	1.06	1.44	0.14	Goeders, 1982
Tellina clam (whole soft)	Orange County outfall	1985	3	4.63	4.70	2.30	6.90	2.30	CSDOC, 1985
Purple-hinge scallop	Palos Verdes - KOU Towers	1976	7	1.50	1.50	1.10	1.99	0.30	Goeders, 1982
	Laguna - Scottsmans Cove	1975	3	1.00	1.00	0.85	1.02	0.10	Goeders, 1982
	Santa Catalina Island	1975	3	1.70	1.85	1.14	2.00	0.50	Goeders, 1982
Black abalone (muscle)	San Clemente Island	1975	5	48.50	52.50	37.80	55.90	7.70	Goeders, 1982
	Palos Verdes - Whites Point	1976	2	19.90	19.85	17.30	22.40	3.60	Goeders, 1982
Market squid (mantle)	Santa Catalina Island	1980	5	0.68	0.76	0.44	0.86	0.17	Goeders, 1982
Ridgeback prawn	Palos Verdes	1980	4	2.90	2.96	2.48	3.23	0.33	Goeders, 1982
	Orange County outfall	1985	7	0.80	0.90	0.26	1.60	0.48	CSDOC, 1985
California spiny lobster	Palos Verdes	1976	4	32.50	47.65	7.00	50.80	19.60	Goeders, 1982
	San Diego area	1977	2	18.60	18.60	16.60	20.50	2.80	Goeders, 1982
	Santa Catalina Island	1976	3	30.90	26.20	13.70	52.70	19.90	Goeders, 1982
Yellow crab	Palos Verdes -Bunker Point	1976	3	29.10	14.70	12.40	60.10	26.90	Goeders, 1982
	Dana Point	1976	2	11.30	11.33	9.27	13.40	2.90	Goeders, 1982
	Palos Verdes-Point Vicente	1974	14	17.29	-	-	-	6.48	Fowler et al 1975
	Santa Barbara	1974	14	51.02	-	-	-	18.43	Fowler et al 1975
Pointer crab (muscle)	Santa Monica Basin	1974	10	6.23	-	2.10	10.08	2.91	Fowler et al 1975
(gonad)	Santa Monica Basin	1974	10	9.19	-	3.79	30.54	9.42	Fowler et al 1975
(digestive gland)	Santa Monica Basin	1974	10	12.24	-	3.27	25.80	7.32	Fowler et al 1975
seastar (pyloric caeca)	Orange County outfall	1985	2	3.50	3.50	3.40	3.60	0.14	CSDOC, 1985
Green sea urchin (gonad)	Orange County outfall	1985	1	3.80	-	-	-	-	CSDOC, 1985
Red sea urchin (gonad)	Palos Verdes Whites Point	1976	3	4.83	4.45	4.26	5.77	0.82	Goeders, 1982
	Corona del Mar	1975	1	1.95	-	-	-	-	Goeders, 1982
	Santa Catalina Island	1976	3	2.43	2.61	1.93	2.76	0.44	Goeders, 1982
	Santa Catalina Island	1975	1	2.29	-	-	-	-	Goeders, 1982
Northern anchovy	LA Harbor Bait Barge	1979	5	0.37	0.32	0.29	0.53	0.10	Goeders, 1982
	Port Hueneme	1980	1	0.89	-	-	-	-	Goeders, 1982
	Oxnard	1980	1	1.25	-	-	-	-	Goeders, 1982
	Huntington Beach	1980	3	2.06	2.02	1.80	2.36	0.59	Goeders, 1982
Pacific sardine	Point Dume	1981	2	0.81	0.81	0.74	0.88	0.10	Goeders, 1982
Striped mullet, adit	Newport Bay	1978	3	0.54	0.58	0.33	0.72	0.20	Goeders, 1982
Striped mullet, juvenile	Newport Bay	1978	3	0.31	0.32	0.28	0.33	0.03	Goeders, 1982
Topsmelt	Newport Bay	1978	3	0.15	0.16	0.15	0.16	0.01	Goeders, 1982
Jack mackerel	San Pedro Channel	1980	2	0.61	0.61	0.51	0.71	0.31	Goeders, 1982
	Santa Catalina Island	1980	1	0.96	-	-	-	-	Goeders, 1982
	Santa Monica bay	1980	1	0.53	-	-	-	-	Goeders, 1982
	Newport	1980	1	0.24	-	-	-	-	Goeders, 1982
Chub (Pacific) mackerel	Orange County outfall	1985	2	0.36	0.36	0.23	0.50	0.10	CSDOC, 1985
	San Pedro Channel	1980	4	0.54	0.57	0.37	0.67	0.13	Goeders, 1982
	Santa Catalina Island	1980	1	0.54	-	-	-	-	Goeders, 1982
Pacific bonito	Redondo	1980	1	0.47	-	-	-	-	Goeders, 1982
	Huntington/Newport	1981	2	0.17	0.17	0.15	0.18	0.02	Goeders, 1982
Barred sand bass	Orange County outfall	1985	2	0.19	0.19	0.11	0.26	0.11	CSDOC, 1985
Spotted sand bass	Newport Bay	1978	3	0.18	0.17	0.12	0.26	0.07	Goeders, 1982
Kelp bass	Palos Verdes	1975	5	2.32	2.00	0.66	4.50	1.39	Goeders, 1982
	Santa Catalina Island	1975	5	2.31	2.16	0.70	4.70	1.61	Goeders, 1982
Striped bass	Newport Bay	1978	3	0.10	0.11	0.08	0.12	0.02	Goeders, 1982
White croaker	Los Angeles Harbor	1979	5	0.82	0.79	0.67	1.00	0.13	Goeders, 1982
	Orange County outfall	1985	1	0.48	-	-	-	-	CSDOC, 1985
Yellowfin croaker	Newport Bay	1978	3	0.25	0.26	0.20	0.29	0.05	Goeders, 1982
Bocaccio	San Clemente Island	1977	3	0.20	0.21	0.13	0.36	0.10	Goeders, 1982
	Palos Verdes West	1973	1	1.50	-	-	-	-	Goeders, 1982
	Palos Verdes	1976	3	0.50	0.36	0.36	0.81	0.30	Goeders, 1982
Scorpionfish	Palos Verdes	1980	4	1.23	1.23	0.74	1.73	0.51	Goeders, 1982
California tonguefish	Orange County outfall	1985	6	0.33	0.37	0.10	0.39	0.11	CSDOC, 1985
Dover sole	Palos Verdes-Point Vicente	1974	11	4.12	-	-	-	1.95	Fowler et al 1975
	Santa Barbara	1974	12	2.43	-	-	-	1.22	Fowler et al 1975
Hornyhead turbot	Orange County outfall	1985	3	1.53	1.40	1.20	2.00	0.42	CSDOC, 1985
Pacific sanddab	Palos Verdes	1976	3	6.36	6.33	5.94	6.84	0.50	Goeders, 1982
	Palos Verdes	1975	1	3.87	-	-	-	-	Goeders, 1982
	Santa Catalina Island	1973	3	10.40	11.10	8.50	11.60	1.70	Goeders, 1982
Speckled sanddab	Orange County outfall	1985	4	0.76	0.77	0.70	0.91	0.10	CSDOC, 1985
California halibut	Los Angeles harbor	1979	4	0.58	0.50	0.42	0.82	0.17	Goeders, 1982
	Palos Verdes	1976	4	0.60	0.64	0.18	0.77	0.30	Goeders, 1982
	San Diego area	1976	2	1.22	1.20	0.79	1.65	0.60	Goeders, 1982
White shark	Santa Catalina Island	1980	1	3.18	3.26	2.94	3.34	0.21	Goeders, 1982
Mako shark	Santa Catalina Island	1980	1	4.67	-	-	-	-	Goeders, 1982
	San Pedro	1980	1	2.81	-	-	-	-	Goeders, 1982
	Newport	1980	3	3.39	4.67	2.46	4.70	1.17	Goeders, 1982

In a recent survey of a few fish taken from Whites Point and outer Los Angeles Harbor, arsenic levels were high (CSDHS, 1991). The CDHS sampled Dover sole, white croaker, and hornyhead turbot in 1986 and discovered highest concentrations of arsenic in muscle of Dover sole from Whites Point (31.6 ppm ww).

Arsenic in composites of livers from Dover sole collected in 1971 and 1972 ranged from 0.88 ppm ww at a site southeast of the Whites Point outfall at Palos Verdes, to 4.3 ppm ww at a site on the seaward side of Santa Catalina Island (from de Goeij and Guinn, 1972a and b). As shown in Figure 4.5, arsenic concentrations were lower in fish from the mainland shelf (range 0.88 to 1.9 ppm ww), including sewage discharge zones (range 0.88 to 1.6 ppm ww), than in fish from an offshore island (range 2.8 to 4.3 ppm ww), suggesting that either arsenic levels were elevated offshore or depressed inshore.

Fish liver was also analyzed for arsenic in the 1984 and 1985 NOAA NS&T Benthic Surveillance surveys. Although Dover sole were not sampled, liver tissue from a related flatfish (hornyhead turbot) was collected at four sites and analyzed for arsenic. The highest mean concentration, 7.32 ppm ww (three composites) occurred at Dana Point, a reference site, and the lowest, 0.62 ppm ww, at San Pedro Canyon on the southern edge of the Palos Verdes Peninsula (Figure 4.6). Arsenic concentrations were intermediate in livers of fish from Santa Monica Bay and San Diego Harbor (3.94 and 2.32 ppm ww, respectively). In contrast to hornyhead turbot, arsenic concentration in livers of white croaker and barred sand bass from Dana Point were no higher than in comparable samples from Seal Beach and San Diego Harbor, respectively (Figure 4.6). Together with the observations of de Goeij et al. (1974), these data may indicate that arsenic concentrations in livers of bottom-dwelling flatfish decrease with proximity to presumably contaminated urban areas.

Although there are no U.S. action limits for arsenic in seafoods, many of the specimens examined contained levels far in excess of the median of 13 international standards of 1.4 ppm ww (range 0.1 to 5.0 ppm ww; Table 4.2). All 71 median concentrations summarized in Table 4.2 exceed the limit of 0.1 ppm ww arsenic set for sardine, tuna, and shellfish by the government of Venezuela (as cited in Nauen, 1983); over half of them (41) exceed the median international standard of 1.4 ppm ww; and 15, mainly for crab, lobster, abalone, kelp (*Macrocystis purifera*), and some sanddabs, exceed the limit of 5.0 ppm ww set for fish, shellfish, or fishery products by the government of Finland.

SUMMARY AND CONCLUSIONS

Limited sediment data suggest that major point or non-point sources of arsenic have resulted in sediment contamination at the Palos Verdes shelf and possibly in the Los Angeles-Long Beach harbors area, with lower concentrations elsewhere including other harbors and waste disposal sites. When last measured, average concentrations in these two areas were 2 to 5 times a presumed background of about 10 ppm dw. Concentrations of arsenic in sediment from Palos Verdes have decreased dramatically (tenfold since 1977) in concert with source control. Beyond these areas, there are generally no strong regional gradients comparable to those exhibited by other contaminants. However, there also remain a paucity of data, especially for bays and lagoons.

There appears to be no correspondence between arsenic in sediments and arsenic in tissues of animals in the Bight. On a regional scale, concentrations of arsenic in many marine organisms are nearly opposite to those in sediments, with lower levels inshore and near urban areas, and higher levels offshore.

The location of the southern California sites with mussels containing higher concentrations (either offshore islands or coastal areas generally removed from major point source discharges and industrial activity) suggests that diffuse mechanisms, such as aerial deposition or oceanic physical processes (upwelling or advection of arsenic-rich oceanic water), may be relatively more important sources for arsenic in mussels than are direct anthropogenic or sediment inputs. This is corroborated by the work of Andreae (1979), who found that arsenate was relatively depleted in the upper waters of southern California and the mid-Pacific Ocean, and enriched below 250 m. Although seawater concentrations of arsenic are usually low, Andreae cited a four order-of-magnitude increase from seawater to marine algae. Papadopoulou (1973), referenced in Eisler (1981), determined that bivalves in the Aegean Sea concentrated arsenic from seawater by factors ranging from 1500 to 46,000. These observations support the possibility of seawater and algal food organisms as significant sources of arsenic to filter-feeding bivalves.
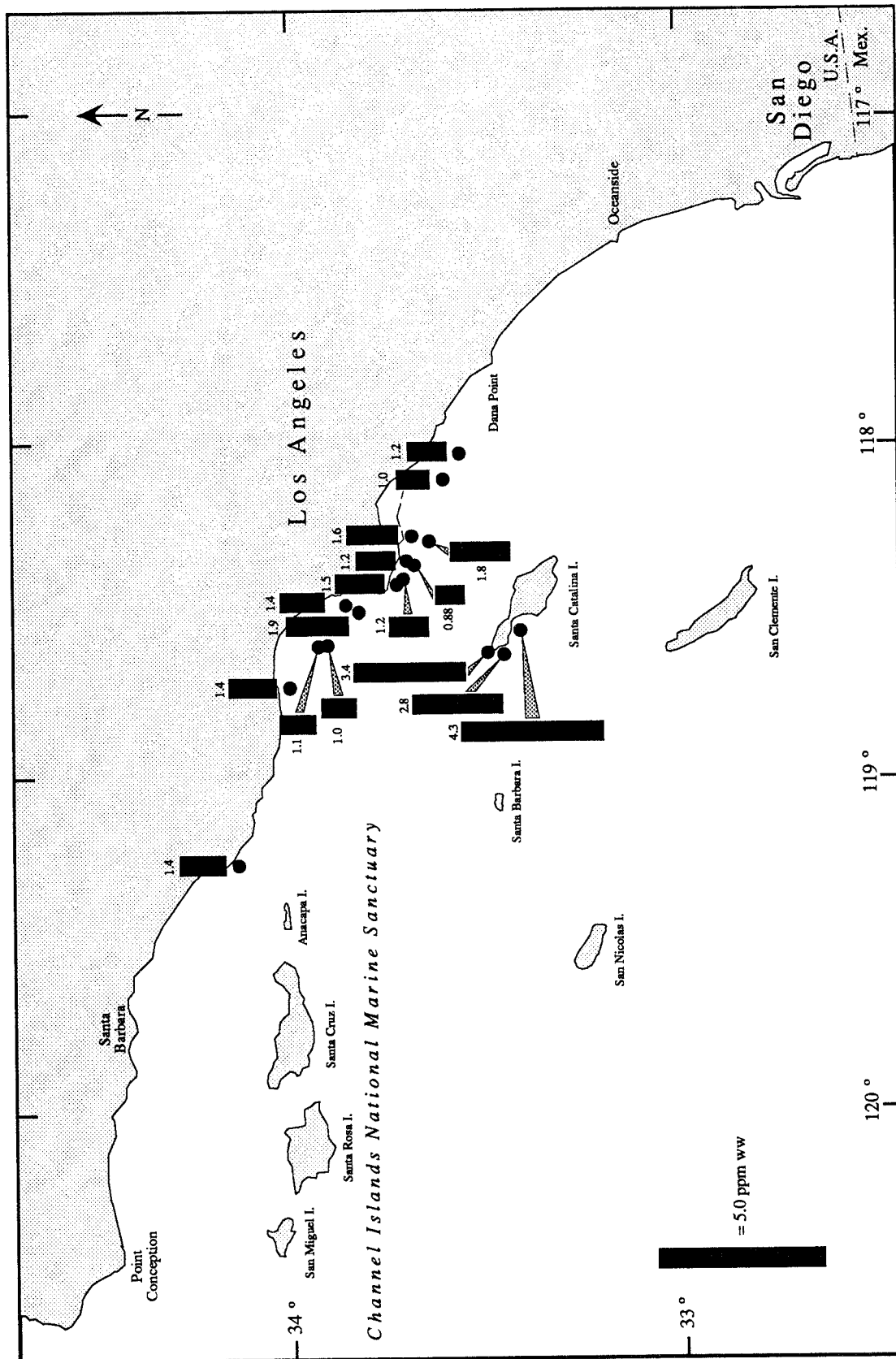
Figure 4.5. Arsenic concentrations in liver tissue of Dover sole collected in the Southern California Bight in 1971-72. Source: De Goeij and Guinn, 1972a and 1972b.
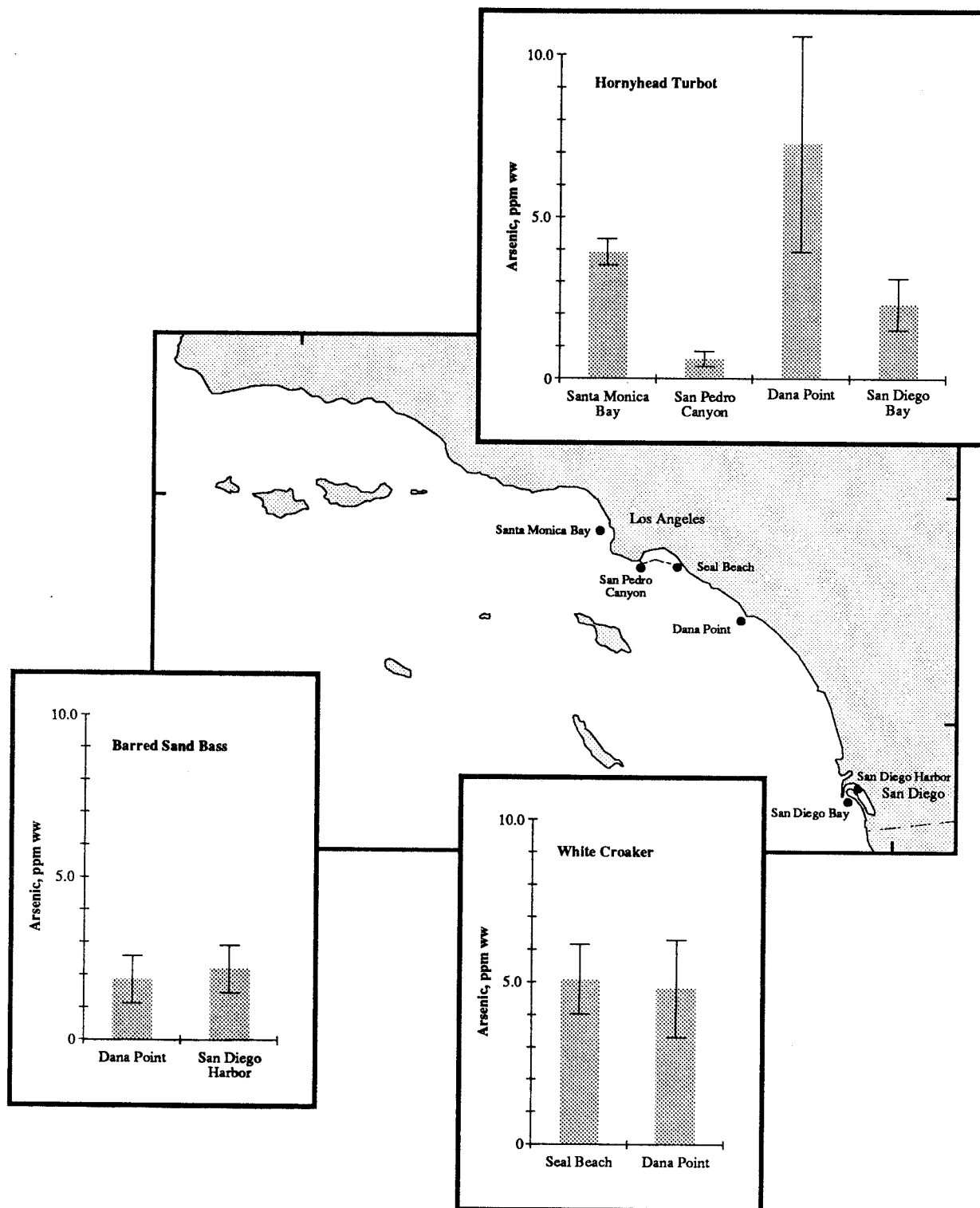
Figure 4.6. Concentrations of arsenic measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

Arsenic occurs in marine organisms of the Bight in concentrations ranging from about 0.1 to over 50 ppm ww. With the noticeable exception of sharks, there is considerable evidence that arsenic concentrations decrease with trophic level, size and/or phylogenetic level, being much lower in muscle tissue of larger fish species than in small fish (anchovy), benthic invertebrates, or mussels (Goeders, 1982). Arsenic concentrations in edible tissues of some fish, squid, lobster, crab, and in liver of some fish were extremely high and exceeded some international criteria and standards. However, high concentrations in these organisms were the same or higher in remote areas compared to urban areas including the Palos Verdes shelf. Therefore, the possibility exists that the source of arsenic to these organisms is "natural."

Due to a nearly complete lack of continuity of species, sites, and tissues among data sets, it is not possible to judge if arsenic concentrations have been changing over time in marine life of the Bight. Similarly, the lack of arsenic measurements in dated cores precludes an assessment of trends in sediment.

INFORMATION NEEDS

In order to put current and future sewage inputs in perspective, data is needed on inputs of arsenic from non-point sources. For example, arsenic should be included among the analytes examined in future surveys of urban runoff.

Arsenic should be measured in dated cores from basins. Surface sediments at previously surveyed sites at Palos Verdes and Los Angeles Harbor should be re-sampled to confirm continued declines in these areas. Subsurface sediments in deep water offshore of Palos Verdes contain higher concentrations than surface sediments and could be a future source of arsenic if the surface is eroded or perturbed. On the other hand, because strong regional arsenic gradients are not apparent in either sediments or organisms, and because of a probable lack of biomagnification, it appears that current anthropogenic inputs of arsenic are insignificant contributions to accumulations in marine life on a regional basis. However, it may be worthwhile re-surveying for arsenic in yellow crab and red sea urchin gonads from near Whites Point (Palos Verdes) to determine if concentrations have decreased relative to reference levels since 1975-77. Likewise, it may be important to explore why arsenic in some species near urban areas has been lower than at island or coastal reference sites. In this connection, it may be important to document the locations and emissions of hydrothermal springs and see if there is any connection to arsenic anomalies in adjacent biota. It is possible that, collectively, submerged hot springs may be major contributors to the background levels along this coast. Finally, it appears that while many southern California organisms exceed the international arsenic standards, this exceedance may be a natural phenomenon. However, to resolve the discrepancy between these international standards and the levels found in southern California organisms, further research to assess health risks to humans that consume seafood contaminated at such levels is necessary, regardless of the source.

CHAPTER 5

CADMIUM

Cadmium is a common trace element widely employed in electroplating applications. It is also used as a component in paint pigments, as a plastic stabilizer, and in batteries (Eisler, 1986a).

According to Aylett (1979), three considerations have made cadmium the focus of environmental concern: It is potentially toxic; it may concentrate in food webs; and it is retained for long periods of time in biological systems. Probably the best-known instance of environmentally induced human cadmium toxicity is that of itai-itai ("ouch-ouch") disease, or osteomalacia, in the Jintzu River basin of Japan following World War II. However, reported cases of cadmium poisoning date back to 1858 (Lauwerys, 1979; Samarawickrama, 1979).

Eisler (1986a) adds several observations of concern. Cadmium concentrates in viscera (kidney and liver), is higher in older organisms, concentrates in biota near point sources, and is higher in marine than in freshwater organisms. Cadmium is incorporated into tissues of zooplankton (*Acartia californiensis*), which may result in recycling of cadmium in surface waters for long periods (Reinfelder and Fisher, 1991). However, data presented here shed doubt on the extent to which cadmium accumulates in marine organisms exposed to cadmium sources.

Cadmium has no known biological function in mollusks. Shellfish, such as mussels, accumulate cadmium from water and subsequently attach it to cadmium-binding peptides such as metallothionein (Frazier, 1979). Cadmium is known to concentrate in mollusk tissue by factors exceeding 10,000, with highest concentrations in digestive gland and kidney (Eisler, 1981). Kluytmans *et al.* (1988) studied the effects of cadmium on reproduction in *M. edulis* and found that concentrations of 100 ppb in seawater significantly inhibited follicle development in both male and female gonads. However, spawning frequency was also stimulated. Although the influences of these opposite effects would result in little net change in the number of gametes released by spawning animals, the authors noted that viability of gametes and embryos and fertilization success were not studied and an overall negative influence on reproduction could in fact result from such exposures to cadmium. Cadmium in sediments is toxic to infaunal organisms. Cadmium also inhibits metabolism of calcium in fish eggs during early development (Meteyer *et al.*, 1988) and this inhibition may lead to bone and eye abnormalities (Rosenthal and Alderdice, 1976).

In 1971, 78 percent (54 mt) of the 69 mt of cadmium entering the Bight was through sewage discharges; most of the balance (14 mt) was from ocean dumping (SCCWRP, 1973). Since then, source control and/or advanced treatment have lowered total inputs from sewage, nearly 6-fold, from a 1974 peak of 55.4 mt to 16.5 mt in 1985 (Figure 5.1; SCCWRP, 1987a and 10 mt in 1987 (SCCWRP, 1988). Runoff from the Los Angeles River carried less than 0.1 mt in 1971 and 1972, 2.7 mt in 1979 and 1980, and 0.3 mt in 1985 and 1986 (Schafer and Gossett, 1988).
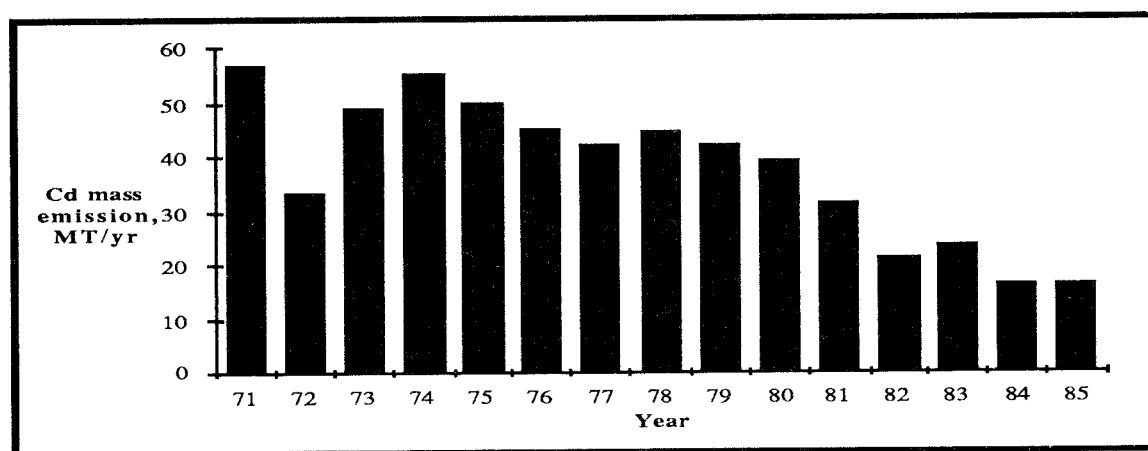
Figure 5.1. Combined mass emissions of cadmium for seven southern California municipal wastewater dischargers, 1971-1985. Source: SCCWRP (1986).

CADMIUM IN SEDIMENTS

Cadmium was analyzed in over 2700 samples of sediment from 1000 stations in 35 survey efforts between 1969 and 1987. Sampling sites were mainly along the southern California mainland shelf over a depth range of 1.5 to 750 m, but also included various bays, lagoons, and harbors. Sediment near islands has rarely been sampled.

According to Katz and Kaplan (1981), the "pollution-free" baseline sediment cadmium concentration is 0.4 ppm dw. By comparison, concentrations of cadmium in selected data sets from southern California harbors, bays, and coastal shelf areas ranged nearly 2000-fold from 0.04 ppm dw at a site along the San Diego County coast sampled in 1985 (Thompson *et al.*, 1987) to 79.0 ppm dw at a site near the Whites Point outfall at Palos Verdes sampled in 1970 (SCCWRP, 1973; Galloway, 1972a and b; Table 5.1). Concentrations in a 1987 SCCWRP synoptic survey of shelf and bay sites ranged from less than 0.05 ppm dw at an intertidal site in Newport Bay to 28.6 ppm dw at the now-abandoned sludge discharge site in Santa Monica submarine canyon (Anderson *et al.*, 1988). Concentration in sediments from rural coastal shelf sites away from sewage discharge zones have ranged from 0.10 to 1.0 ppm dw, with survey medians ranging from 0.10 ppm dw along the San Diego County coast (Thompson *et al.*, 1987), to 0.051 ppm dw between Newport and Dana Point (Word and Mearns, 1979). Shelf sites near outfalls contained cadmium concentrations ranging from 0.13 to 79.0 ppm dw, with survey medians ranging from 0.26 near Oxnard to 15.2 ppm dw at Palos Verdes (SCCWRP, 1973). Bay and harbor concentrations have ranged from 0.05 to 15.5 ppm dw, with survey medians ranging from 0.10 for the mouth of the Tijuana Estuary (Gersberg *et al.*, 1989) to 3.49 in Los Angeles-Long Beach harbors in 1973 (Chen and Lu, 1974). Median concentrations at three stations monitored in Lower Newport Bay in 1985-88 were 1.1 ppm dw with station means ranging from 0.75 ppm dw in the Rhine Channel to 1.8 ppm dw in the western turning basin (OCEMA, 1989).

Results of the NOAA NS&T Program support Katz and Kaplan's (1981) background cadmium levels. The national mean sediment cadmium level measured between 1984 and 1989 was 0.398 ppm dw (median, 0.219 ppm dw).

Although 0.4 ppm dw may represent a recent estimate of cadmium in pollution-free sediments (Katz and Kaplan, 1981), sediment cadmium concentrations appear to vary greatly with water depth and depth-related factors (grain size, organic content) such that there may be no single "normal" value. In a survey of trace contaminants at 65 stations along the relatively unpolluted coastal shelf between Point Dume and Port Hueneme, (Hershelman *et al.*, 1982) surficial sediment cadmium concentrations ranged over 20-fold from 0.12 ppm dw at a 20-m deep site near Point Dume to 2.8 ppm dw at a nearby 700-m deep site off the Ventura-Los Angeles county boundary. Median concentrations ranged one order of magnitude from 0.22 ppm dw along the 20-m isobath to 2.0 ppm dw along the 700-m isobath. Correlations were highly significant ($p<0.001$) and positive with depth ($r = 0.841$), total volatile solids ($r = 0.791$), and percent silt ($r = 0.882$) and inverse with dry weight (solids, $r = -0.848$).

Assuming a background concentration of 0.4 ppm dw, then elevations above background among different areas during recent surveys ranged from 27.5 at Palos Verdes (1985) to 0.25 (one-quarter background) for several stations along the coast between Newport Beach and Dana Point (Table 5.2). Additional areas with median concentration exceeding 3 times background included Santa Monica Bay 60-m sites (8.8 times) and San Diego Harbor (4.5 times).

Table 5.1. Mean, median, minimum, and maximum cadmium concentrations in surface sediment from selected surveys, 1970-1985 in ppm dw.

Site	Year	N	Mean	Median	Min	Max	SD	Source
Rural Coastal Shelf (60 meters only):								
Santa Barbara shelf	1977	11	0.48	0.46	0.20	0.94	0.22	1
	1985	4	0.2	0.2	0.2	0.2	0.0	2
Port Hueneme to Point Dume	1977	4	0.43	0.41	0.21	0.70	0.22	1
	1980	11	0.54	0.49	0.13	1.00	0.27	3
	1985	2	0.2		0.1	0.3	0.1	2
Newport to Dana Point	1977	3	0.67	0.51	0.47	1.04	0.32	1
	1978	6	0.27	0.26	0.10	0.42	0.14	4
	1985	1	0.1					2
Outfall Areas:								
Oxnard shelf	1971a	4	0.26	0.26	0.17	0.35	0.074	9
Santa Monica Bay	1970a	24	1.48	1.04	0.19	7.7	1.56	9
	1977b	13	1.46	0.65	0.45	5.10	1.53	1
	1978b	31	2.84	2.20	0.15	8.80	2.44	4
	1985b	3	3.0	3.5	1.0	4.4	1.8	5
Palos Verdes shelf	1970a	22	19	14	0.63	79	20	9
	1977b	8	18	15	0.15	60	20	1
	1978b	8	15	15	1.20	28	9.57	4
	1985b	10	12	11	0.3	27	8.8	6
Orange County shelf	1970a	13	1.6	0.92	0.28	7.6	2.1	9
	1977b	11	0.91	0.60	0.25	3.50	0.93	1
	1978b	12	0.53	0.45	0.13	1.50	0.42	4
	1985b	9	0.9	0.6	0.2	3.9	1.2	7
Point Loma shelf	1970a	5	0.51	0.4	0.33	0.92	0.23	9
	1977b	6	0.68	0.66	0.50	0.97	0.16	1
	1985b	7	1.2	1.1	1.1	1.7	0.2	8
Bays and Harbors:								
Marina del Rey[a]	1977	11	0.7	0.6	0.1	1.2	0.3	10
	1978	11	0.5	0.5	0.2	0.8	0.2	10
	1984	12	0.5	0.5	0.5	0.5	0.0	11
	1985	12	0.5	0.5	0.5	0.5	0.0	12
	1987	13	1.4	0.5	0.5	5.8	1.5	13
Los Angeles-Long Beach harbors a	1973	31	3.74	3.49	0.70	7.18	1.68	14
	1978	31	0.76	0.62	0.23	2.62	0.51	15
Upper Newport Bay[a]	1971	3	1.60	1.80	0.1	3.0	1.5	18
Lower Newport Bay[a]	1971	7	1.3	1.4	0.6	2.3	0.63	18
Upper Newport Bay[a]	1980	8	1.60	0.84	0.35	6.60	2.06	16
San Diego Harbor	1974	11	3.42	2.43	0.25	11.2	2.92	18
San Diego Harbor[a]	1983	20	2.8	1.8	0.5	16	3.9	17
Tijuana Estuary, mouth	1988	5	0.10	0.11	0.05	0.14	0.03	19
Tijuana Estuary, north arm	1988	14	0.44	0.17	0.09	1.85	0.60	19
Tijuana Estuary, south arm	1988	26	1.08	0.78	0.05	3.52	1.10	19
OVERALL					0.05	79		

[a] - all depths; [b] - 60-m only

REFERENCES:

1 Word and Mearns, 1979
2 Thompson et al., 1987
3 Hershelman et al., 1982
4 Hershelman et al., 1981
5 Hyperion Treatment Plant, unpublished data
6 CSDLAC, unpublished data

7 CSDOC, unpublished data
8 CSD, unpublished data
9 SCCWRP, 1973 (Galloway, 1972 a and b)
10 Soule and Oguri, 1980
11 Soule and Oguri, 1985
12 Soule and Oguri, 1986

13 Soule and Oguri, 1987
14 Chen and Lu ,1974
15 Soule and Oguri, 1978
16 MBC and SCCWRP, 1980
17 Ladd et al., 1984
18 Young et al., 1975
19. Gersberg et al., 1989

Table 5.2 Median sediment cadmium concentrations and ratios to reference (0.4 ppm dw) concentration for most recent surveys in 16 coastal areas, bays, or harbors in the Southern California Bight.

Area	Year	Median	Ratio to Reference
Palos Verdes shelf [b]	1985	11.0	27.5
Santa Monica Bay [b]	1985	3.5	8.8
San Diego Harbor	1983	1.8	4.5
Lower Newport Bay [a]	1985-88	1.1	2.7
Point Loma shelf [b]	1985	1.1	2.7
Upper Newport Bay	1980	0.84	2.1
Tijuana Estuary, south arm	1988	0.78	2.0
Los Angeles-Long Beach harbors	1978	0.62	1.5
Orange County shelf [b]	1985	0.60	1.5
Marina del Rey	1985	0.53	1.2
Bolsa Bay	1980	0.45	1.1
Santa Barbara shelf [b]	1985	0.20	0.5
Port Huneme to Point Dume, shelf [b]	1985	0.20	0.5
Tijuana Estuary, north arm	1988	0.17	0.43
Tiguana Estuary, mouth	1988	0.11	0.28
Newport to Dana Point, shelf [b]	1985	0.10	0.25

[a] Data from OCEMA, 1989. All other data cited in Table 5.1.

[b] 60-m depth only; otherwise, all depths

Sampling at only one depth, the 1977 SCCWRP 60-m survey yielded surface sediment cadmium concentrations ranging from 0.2 ppm dw at sites off Pitas Point north of Ventura and Trancas Canyon (west of Santa Monica Bay) to 60.8 ppm dw at a site near the Whites Point outfall at Palos Verdes (Figure 5.2). Prominent but small-scale peaks were apparent from high concentrations near outfalls in Santa Monica Bay and off northern Orange County as well as from the very high concentration center at Palos Verdes (Figure 5.2). Combined data from 60-m sites sampled by Thompson *et al.* (1987) and four discharge monitoring programs indicated that similar patterns of cadmium prevailed during the summer of 1985 (Figure 5.3). A major difference however, was that concentrations at the 60-m isobath were considerably lower at Palos Verdes in 1985 compared to the 1977 or to an earlier 1970 survey (by SCCWRP, 1973; Galloway, 1972a; 1979).

The concentration gradients apparent from these previous surveys were also reflected in sediment samples from 1984-86 NOAA NS&T Program surveys (Figure 5.4). However, concentrations were generally lower in urban areas in these surveys than in previous surveys, possibly because sites were remote from point sources and were shallower, but differences in methods may also have contributed to these differences.

There appears to be an along-shore gradient of cadmium in sediments. As illustrated in Figures 5.2 and 5.3, data from both the 1977 and 1985 SCCWRP Synoptic surveys along the 60-m isobath indicated that, excluding areas directly impacted by outfall discharges, sediment cadmium concentrations along the coastline northwest of the Palos Verdes peninsula (Point Conception to Trancas Canyon) were higher than those southeast of the peninsula and San Pedro Bay (Corona del Mar to La Jolla). Application of the nonparametric Mann-Whitney test indicated that in both surveys, the northwestern group of cadmium concentrations were significantly higher than the southeastern grouping (p=0.025). As noted below, a similar relationship appeared to exist in distribution patterns of cadmium in mussels.

Figure 5.2. Cadmium concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line, based on data from the 60-m Control Survey performed from April through August 1977 (Word and Mearns, 1979).
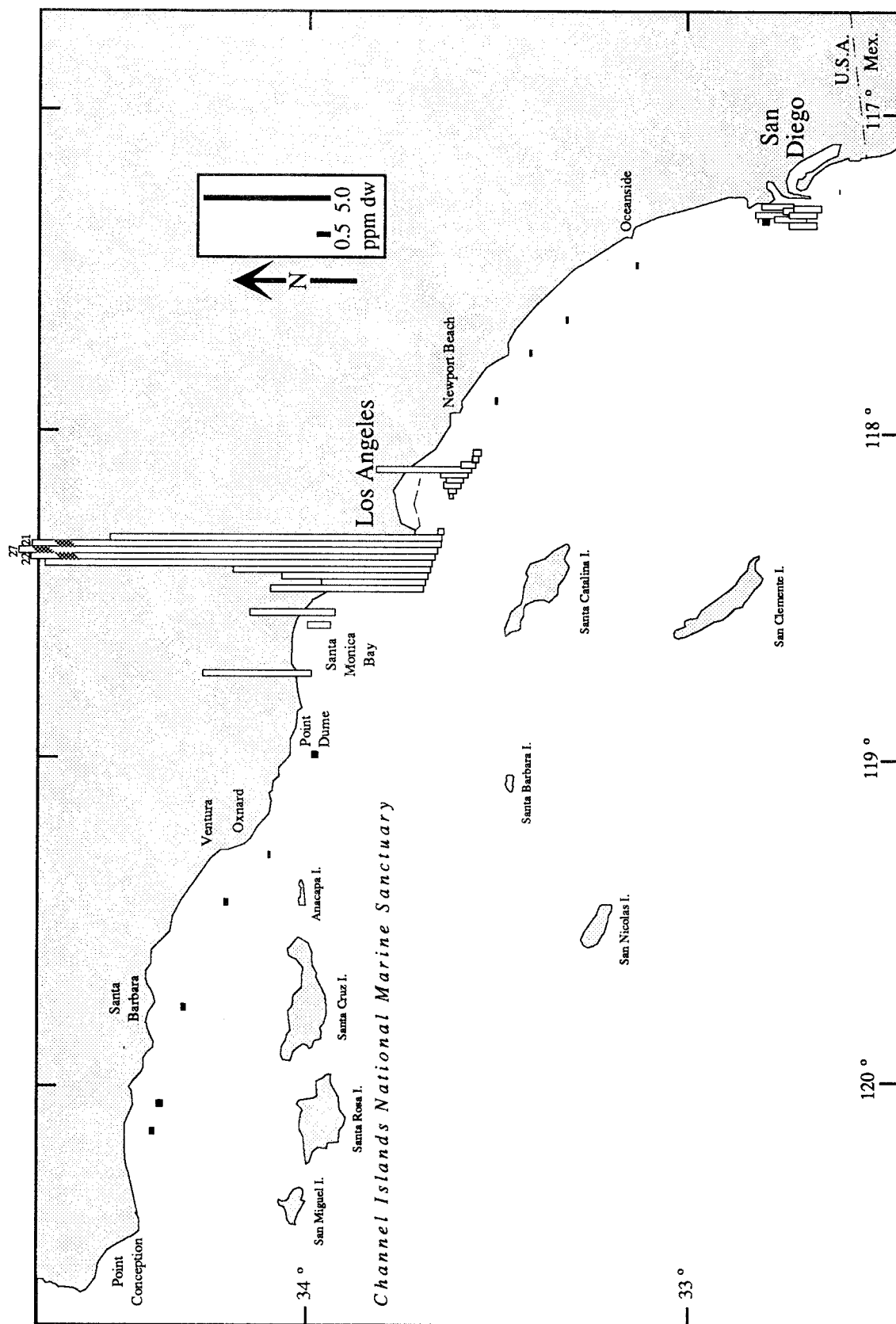
Figure 5.3. Cadmium concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line for 1985; the black bars are based on data derived from Thompson *et al.*, 1987, while the white bars are based on data obtained from the various sanitation districts (City of Los Angeles, Los Angeles, Orange, and San Diego counties).
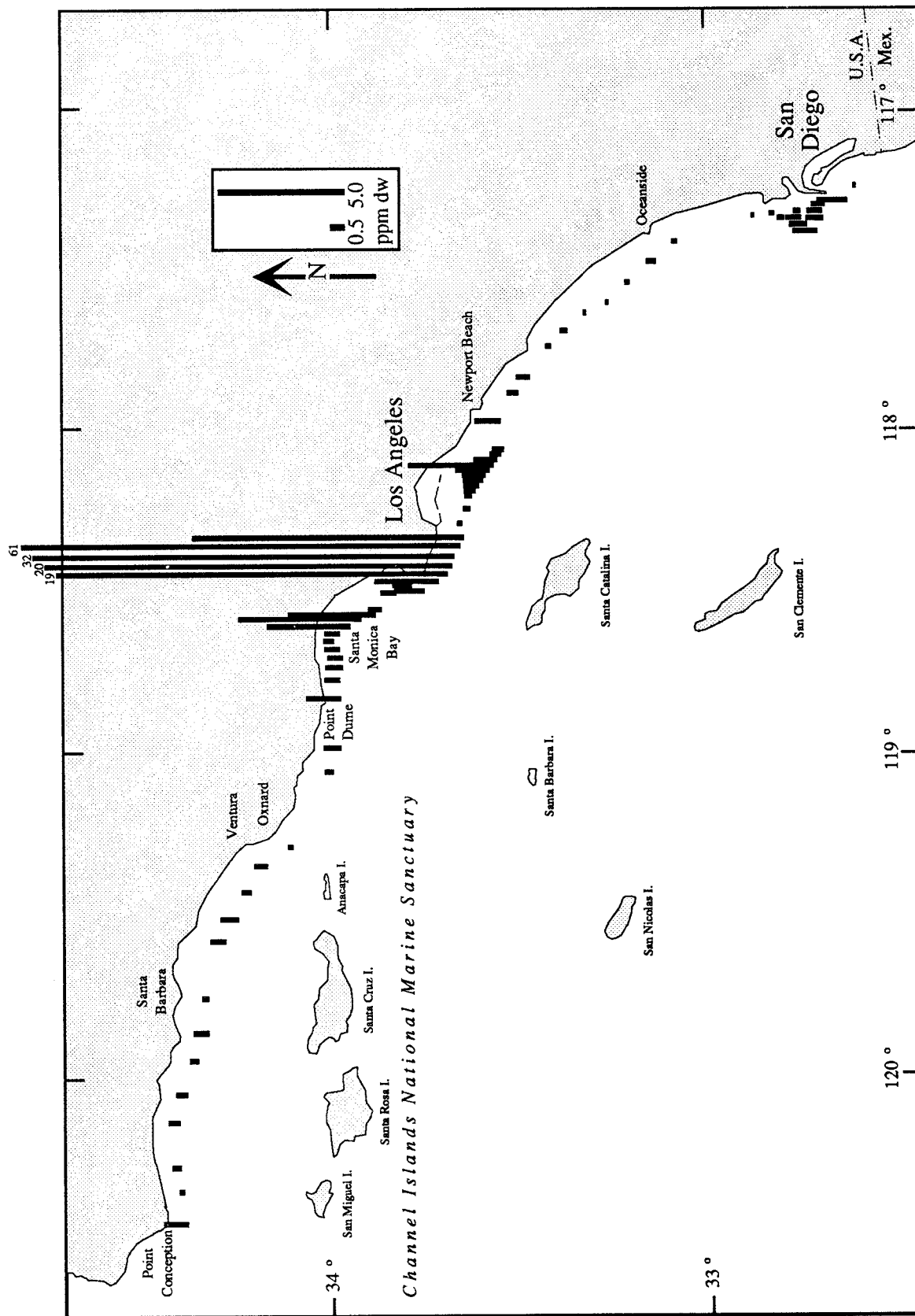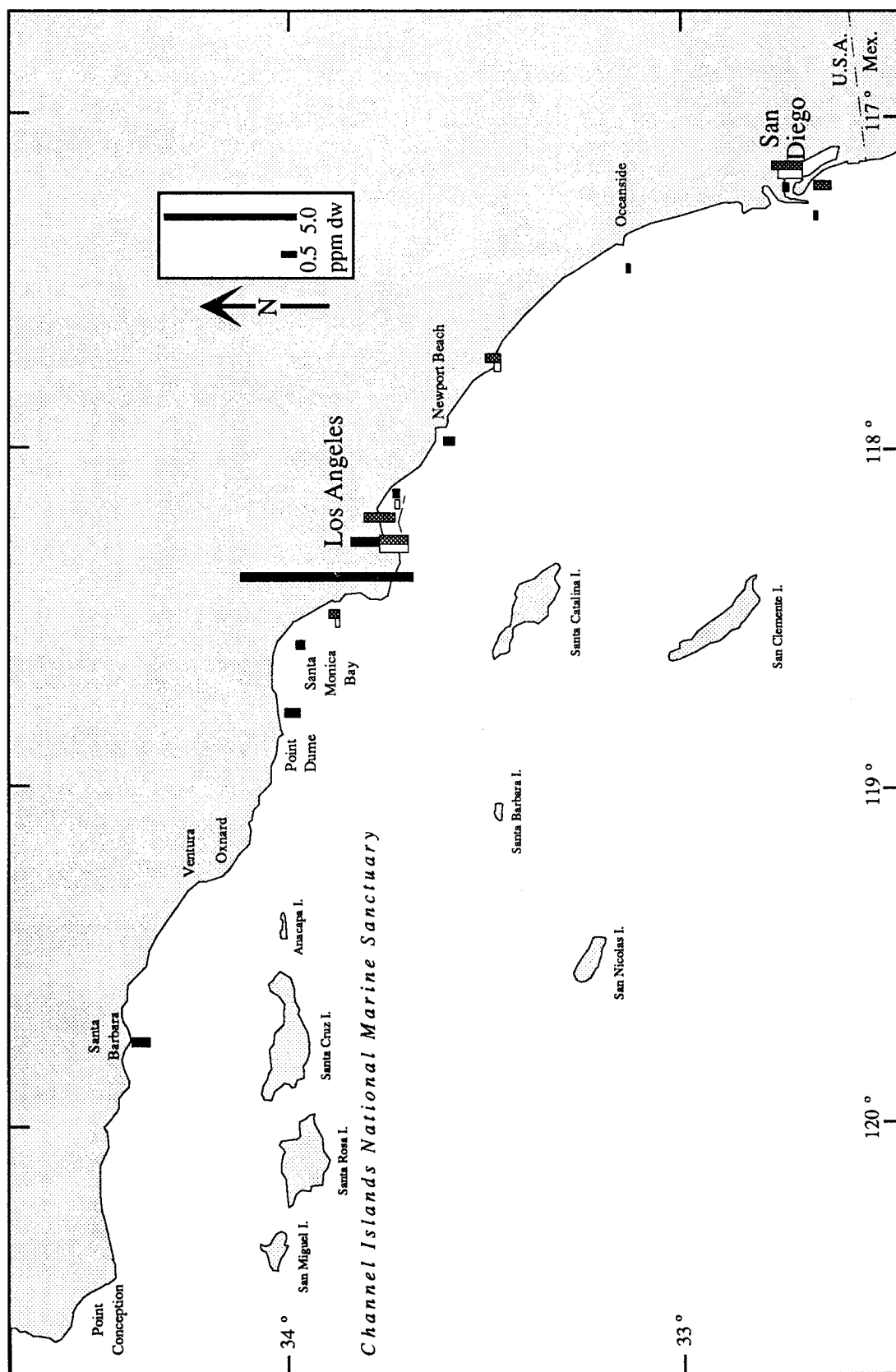
Figure 5.4. Cadmium concentrations in the surficial sediments of the Southern California Bight based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 (□) and 1985 (▦) and Mussel Watch Project for 1986 (▮) (NOAA, 1988 and unpublished data).

In one study, 10-day median LC_{50} value for a marine amphipod was 9.8 ppm dw and EC_{50} values (based on emergence and reburial) were 9.7 and 9.07 ppm dw, respectively (Mearns et al., 1986). In another study under similar conditions, the median LC_{50} was 6.9 ppm dw and the EC_{50} for reburial was 6.4 ppm dw (Swartz et al., 1985). In that study, the highest concentration for which there was no evidence of acute effects was 2.0 ppm dw. In addition, toxicity was due exclusively to cadmium dissolved in interstial water (up to 4.4% of total sediment cadmium) and not to sediment-bound cadmium. Finally, it was demonstrated that increasing organic content of sediment, through the addition of sewage sludge, decreased toxicity (Swartz et al., 1985). Swartz et al., (1985; 1986) reported that concentrations less than 9 to 10 ppm dw at Palos Verdes were not associated with sediment toxicity to test amphipods (Rhepoxynius abronius).

In a national review of concentrations of cadmium in sediment associated with adverse biological effects, Long and Morgan (1990) calculated a probable effects range (ER-L to ER-M) of 5 to 9 ppm dw. Sites at the Palos Verdes Peninsula were the only sites that exceeded these values. However, a recent study by DiToro et al. (1990) suggests that when sediment acid volatile sulfide (AVS) concentrations are used to normalize the sediment cadmium concentration, the resulting ratio is a good predictor of toxicity to two amphipod species (Ampelisca abdita and Rhepoxynius hudsoni). Total mortality occurred when the ratio of cadmium to AVS (on a molar basis) was greater than 3. DiToro et al. (1990) suggest that because cadmium binds to sulfides, the amount of AVS in sediment controls cadmium's availability to marine organisms.

Independent monitoring surveys by CSDLAC clearly confirmed that cadmium in surface sediments at nine sites along the 60-m isobath at Palos Verdes decreased 71 percent during the 12-year period 1974 through 1985 (Figure 5.5). The decline (from a median of 47 ppm dw in 1974 to 20 ppm dw in 1980) was due almost exclusively to source control (Stull and Baird, 1985). Therefore, although the highest coastal sediment cadmium concentrations in 1985 existed at Palos Verdes, concentrations along the 60-m isobath experienced a 4- to 5-fold decline since the early 1970s.

Cadmium concentrations in surface sediment within the impact zone of the diffuser of the Orange County Sanitation Districts ocean outfall (5 miles off Huntington Beach) were low (less than 1 ppm dw) but nonetheless experienced a long-term decline between 1978 and 1985 coincident with decreased emissions (CSDOC, 1986).

Historically, data from dated sediment cores from deep offshore basins indicate that cadmium was not a regionwide contaminant until the 1960s when concentrations increased slightly (25%) in the Santa Barbara Basin (Bruland et al., 1974). Recently collected cores from the Santa Barbara Basin suggest inputs have decreased during the 1970s and 1980s (Schmidt and Reimers, 1987) a trend consistent with the observations at Palos Verdes (Stull and Baird, 1985). There has been no excess accumulation of cadmium south and southeast of Los Angeles at a core site near San Clemente Island (Bertine and Goldberg, 1977) nor in the Soledad Basin off southern Baja California (Bruland et al., 1974). Thus, cadmium of anthropogenic origin was only a regionwide contaminant for a brief period (1960s).
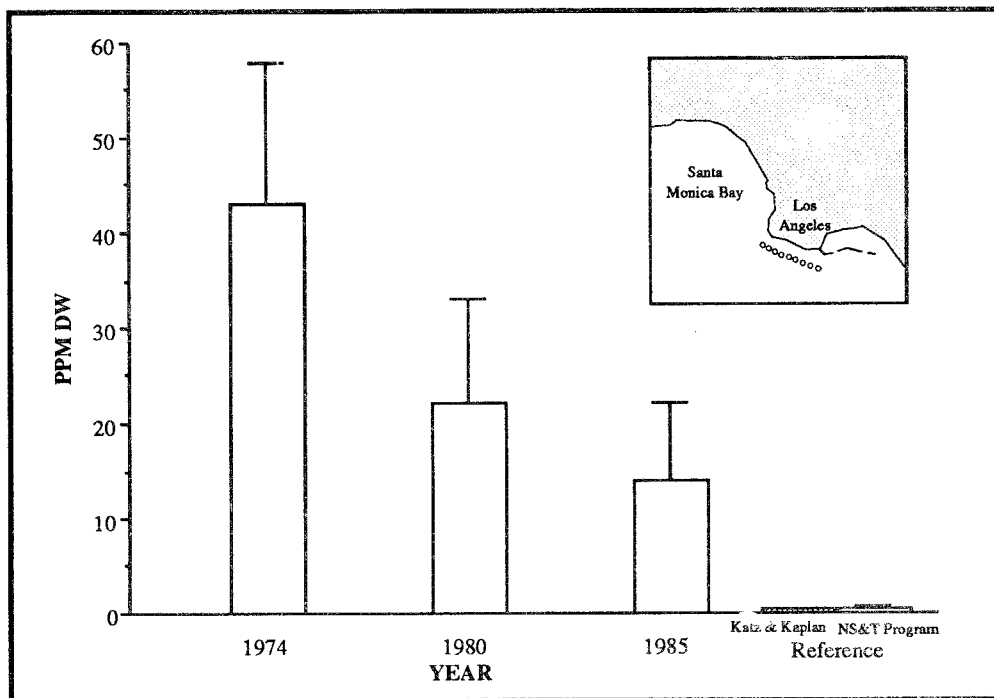
Figure 5.5. Mean cadmium concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC. The reference values are based on the value reported by Katz and Kaplan (1981) and the mean of four relatively isolated NOAA NS&T Program sites in the Southern California Bight sampled between 1984 and 1986 (NOAA, 1988 and unpublished data). Inset shows approximate locations of sites sampled by CSDLAC.

CADMIUM IN MUSSELS

Cadmium has been measured in hundreds of mussel samples from the Bight in several series of surveys beginning in 1971. Results for concentrations of cadmium in mussel tissue collected in the Southern California Bight suggest two patterns of regional distribution. Body burdens of many contaminants are well-correlated to centers of population and industrial activities, and cadmium levels in mussels appear to demonstrate this pattern in *M. edulis* collected within the urban harbors of the Southern California Bight. However, concentrations in *M. californianus* do not support a connection between proximity to anthropogenic sources and high tissue levels. Figures 5.6 to 5.8 illustrate results on a Bight-wide basis for four surveys. Results are differentiated by species (*M. californianus* in contrast to. *M. edulis*) and tissue types.

In a 1971 SCCWRP survey, cadmium in digestive gland of *M. californianus* ranged from 5.7 ppm dw in samples from near Newport Beach to 29 ppm at Point Dume (Figure 5.6). Although no large-scale gradient was evident, low concentrations (less than 12 ppm dw) occurred only near urban sites (Santa Monica, Palos Verdes, and Newport Bay), whereas high concentrations (more than 20 ppm dw) occurred near both urban areas and at some offshore islands. Similarly, a 1977 CMW survey of whole mussels (minus gonads) indicated high concentrations (5 to 12 ppm dw) occurred at offshore islands and lower concentrations (1.4 to 3.1 ppm dw) off the mainland coast (Figure 5.7). In the 1986 NOAA NS&T Mussel Watch Survey, cadmium also appeared to demonstrate low (less than 6.0 ppm dw) concentrations in *M. californianus* (Figure 5.8).
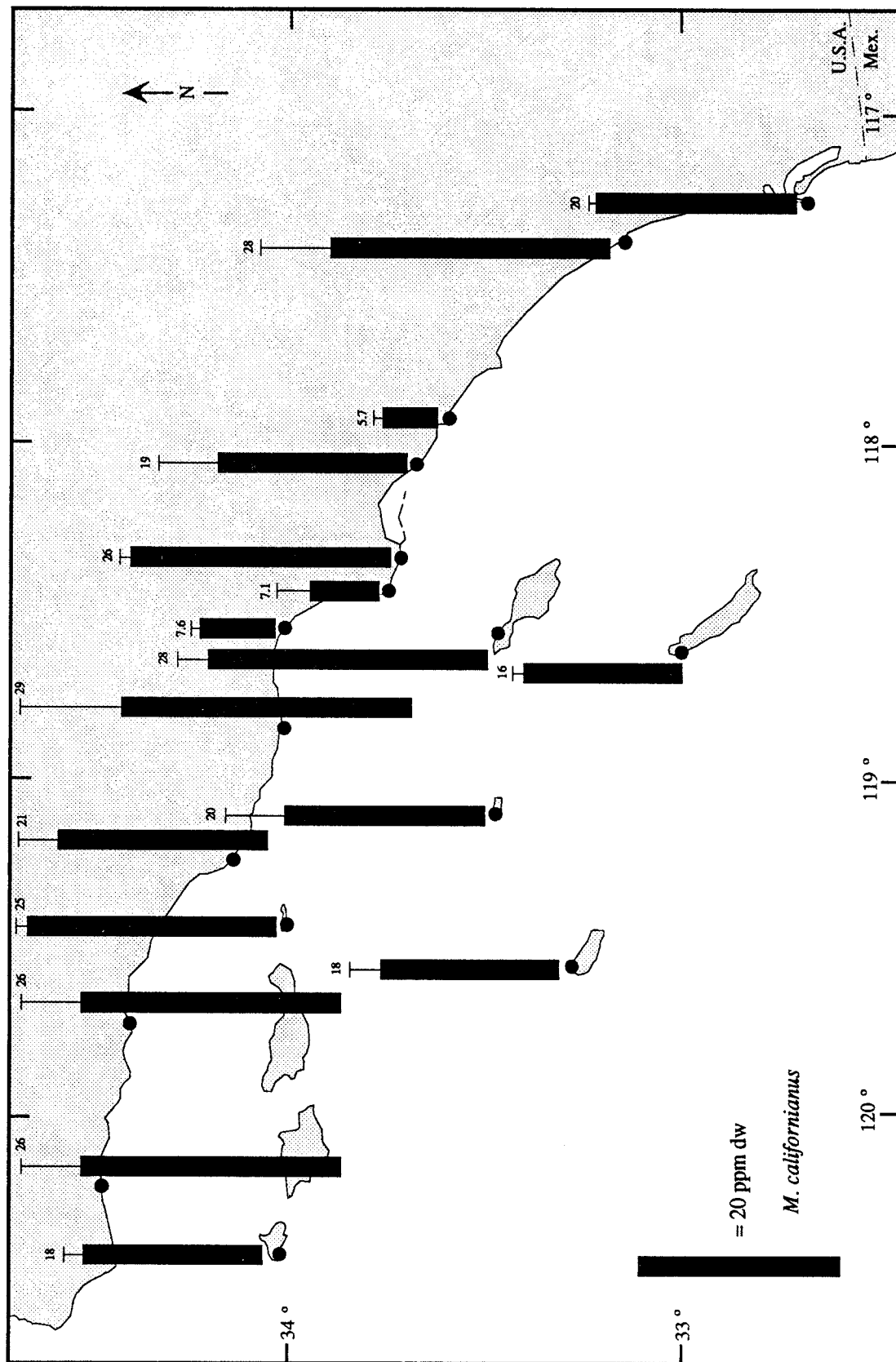
Figure 5.6. Cadmium in digestive gland of mussels sampled in 1971. Values shown are means of six samples, each sample = one individual.
Source: Young, 1974.
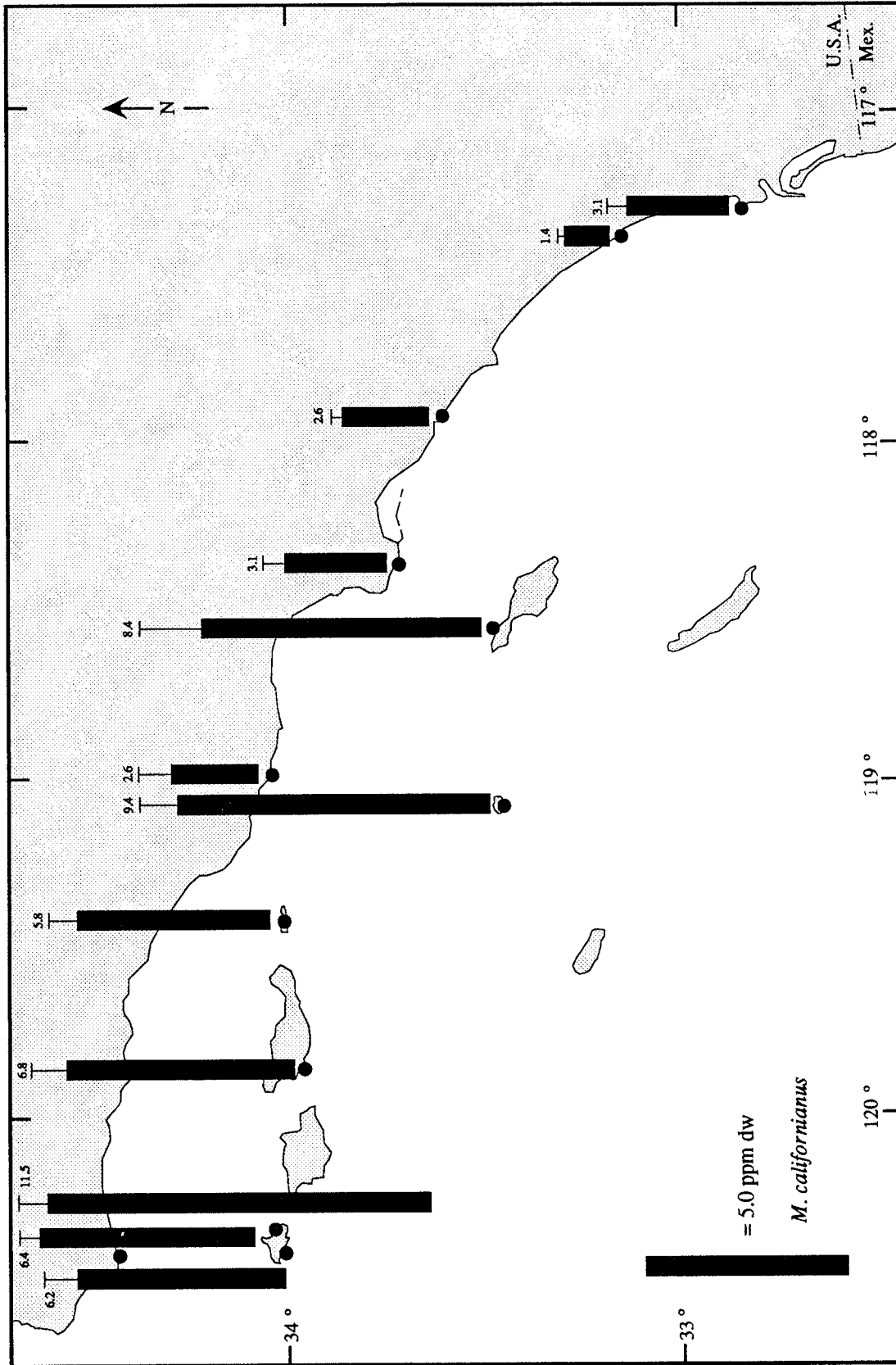
Figure 5.7. Cadmium in whole soft body tissue, less gonads, of mussels sampled in the Southern California Bight in 1977. Source: Phillips, 1988.
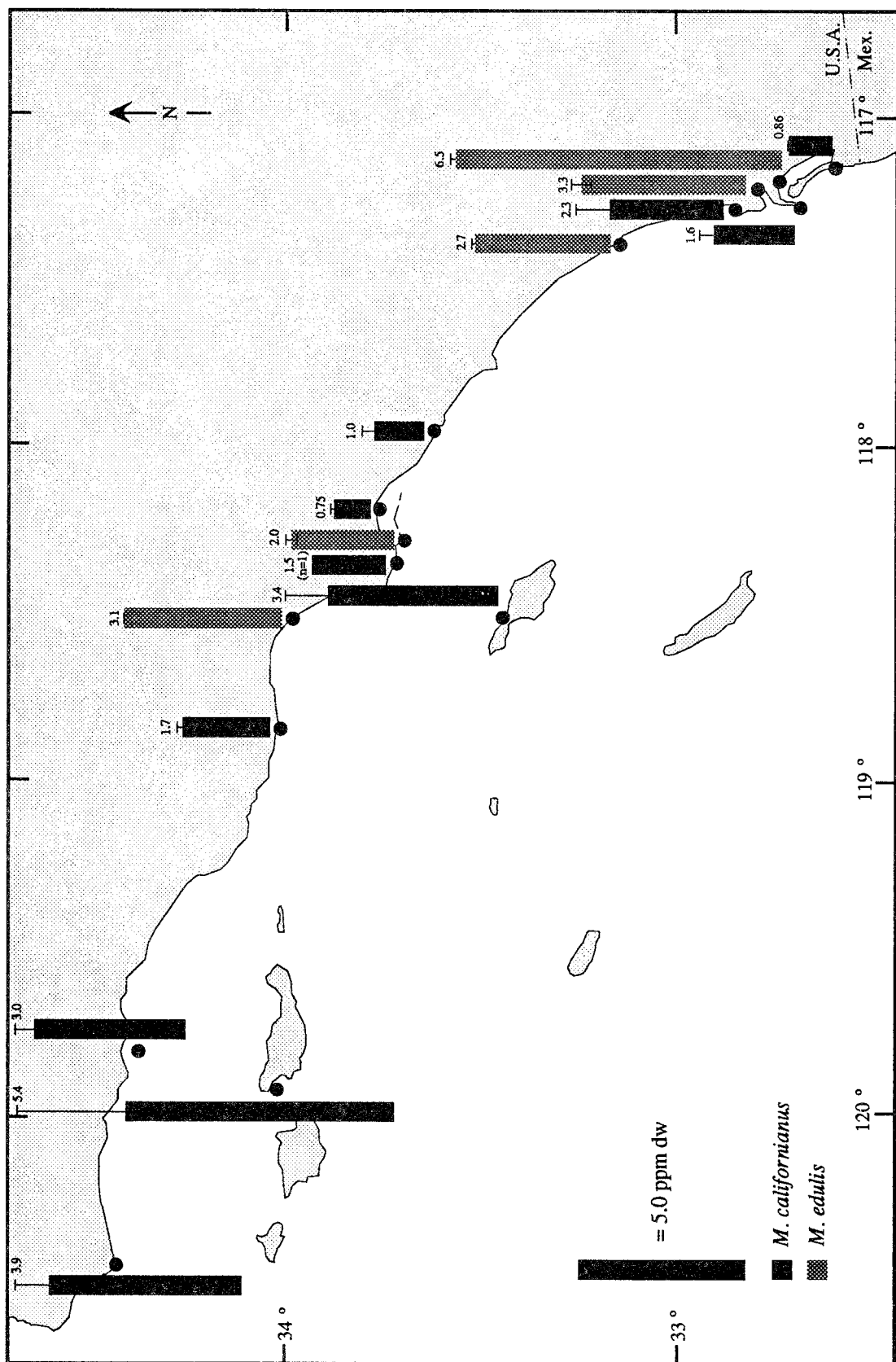
Figure 5.8. Cadmium in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

Table 5.3 and Figure 5.9 summarize survey data for *M. californianus*, which prefers exposed and rocky habitats and are more widely distributed in the region. When sites are classified into the three general categories of offshore island, non-urban mainland, and urban mainland, within-survey mean values generally agree with the distributional pattern described above, with higher concentrations found at offshore island sites (4.4 to 20.8 ppm dw). In the CMW Program and the NS&T Mussel Watch Project, non-urban locations were intermediate (4.1 and 2.5 ppm dw, respectively) and coastal urban sites had the lowest tissue cadmium concentrations (2.6 and 0.94 ppm dw, respectively). In the 1976-78 EPA Mussel Watch program, and the 1971 SCCWRP sampling, differences among the three site types were less distinct (Figure 5.9).

Table 5.3. Summary of results for cadmium in coastal mussel tissue for four survey efforts in the Southern California Bight.

Survey	Year	Site Type	N	Cd in tissue mean, ppm dw	Standard deviation
California Mussel Watch	1977-78	Offshore Island	26	7.8	2.62
		Non-urban Coastal	9	4.1	1.46
		Coastal Urban	15	2.6	0.78
NS&T Mussel Watch	1986	Offshore Island	6	4.4	1.84
		Non-urban Coastal	15	2.5	0.96
		Coastal Urban	10	0.94	0.26
EPA Mussel Watch	1976-78	Offshore Island	3	6.2	2.11
		Non-urban Coastal	6	2.0	0.74
		Coastal Urban	5	2.3	1.87
SCCWRP	1971	Offshore Island	6	20.8	4.66
		Non-urban Coastal	2	18.7	6.36
		Coastal Urban	9	19.9	9.21

NOAA's NS&T Mussel Watch results for 1986-89 were evaluated for correlations between levels of cadmium and PCBs or DDT. An analysis of scatter plots suggested a curvilinear relationship existed. Table 5.4 presents Pearson product moment correlation values for log transformed concentrations in both mussel species nationwide and north and south of Point Conception. Although results of this analysis varied, there is some evidence to suggest that levels of DDT and cadmium are negatively correlated in mussels south of Point Conception and in *M. californianus* along the Pacific Coast of the United States (Figure 5.10).

Despite the absence of a regionwide coastal contamination gradient related to mainland sources, anthropogenic inputs of cadmium may be of importance in more localized situations. For example, the highest concentrations in *M. edulis* occur at the innermost locations within harbors (Figures 5.11, 5.12, and 5.13). Among these harbor surveys, ranges of tissue cadmium were from 0.83 to 4.6 ppm dw in 1982 CMW whole samples of *M. edulis* from the Los Angeles-Long Beach harbors area (Figure 5.13), and from 1.9 to 18.0 ppm dw in a 1974 SCCWRP mussel digestive gland survey of the San Diego Harbor area (Figure 5.11). In the Los Angeles-Long Beach harbors area, concentrations were higher at inner harbor sites (1.4 to 4.6 ppm dw) than in outer harbor sites (0.83 to 2.1 ppm dw; Figure 5.13). These data support a similar pattern observed in a 1974 SCCWRP survey (Figure 5.12). Among the five *M. edulis* sites in the NOAA NS&T 1986 sampling, the highest concentration occurred at Harbor Island in San Diego Harbor (6.5 ppm dw), with lower concentrations (2.0 to 3.3 ppm dw) at other sites (Figure 5.8).
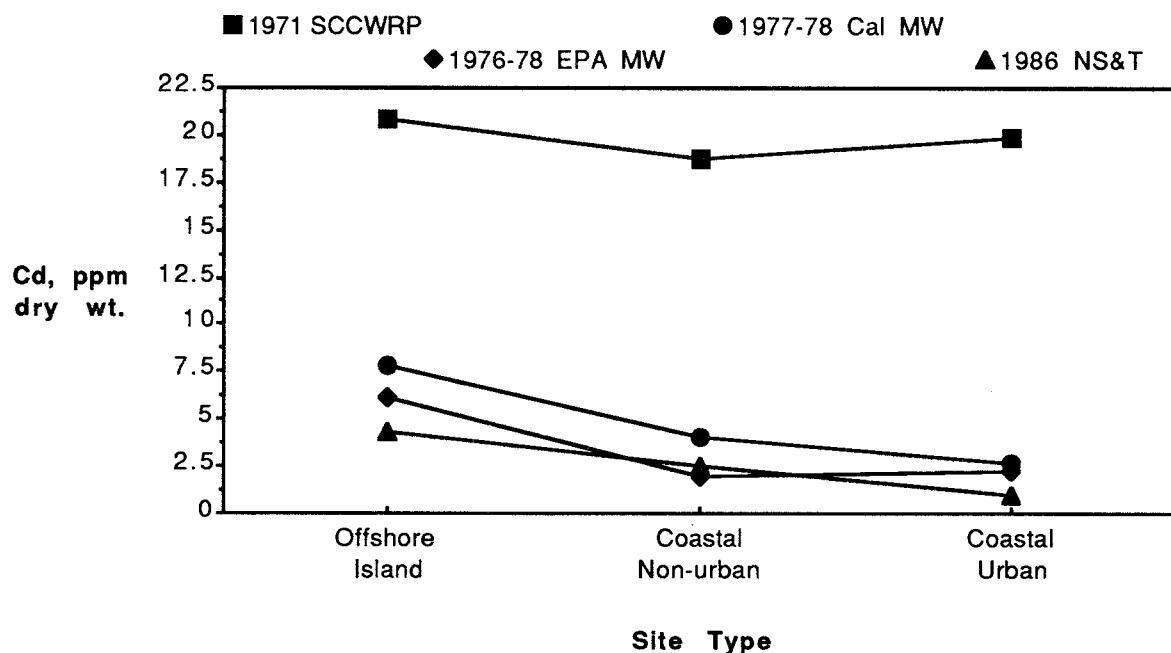
Figure 5.9. Cadmium in coastal mussels collected in the Southern California Bight by general site type. Data from Table 5.2.

Table 5.4. Pearson product moment correlation (r) values for cadmium in mussels vs. PCB or DDT in mussels (log transformed) 1986-89.

	Log cadmium *M. edulis* Nationwide n = 658	Log cadmium *Mytilus* spp. north of Point Conception n = 351	Log cadmium *Mytilus* spp. south of Point Conception n = 190	Log cadmium *M. californianus* Pacific Coast n = 292
Log PCB	0.043	0.068	-0.066	-0.45*
Log DDT	0.18*	0.157*	-0.424*	-0.636*

* significant at $\alpha = 0.05$ (Zar, 1984)
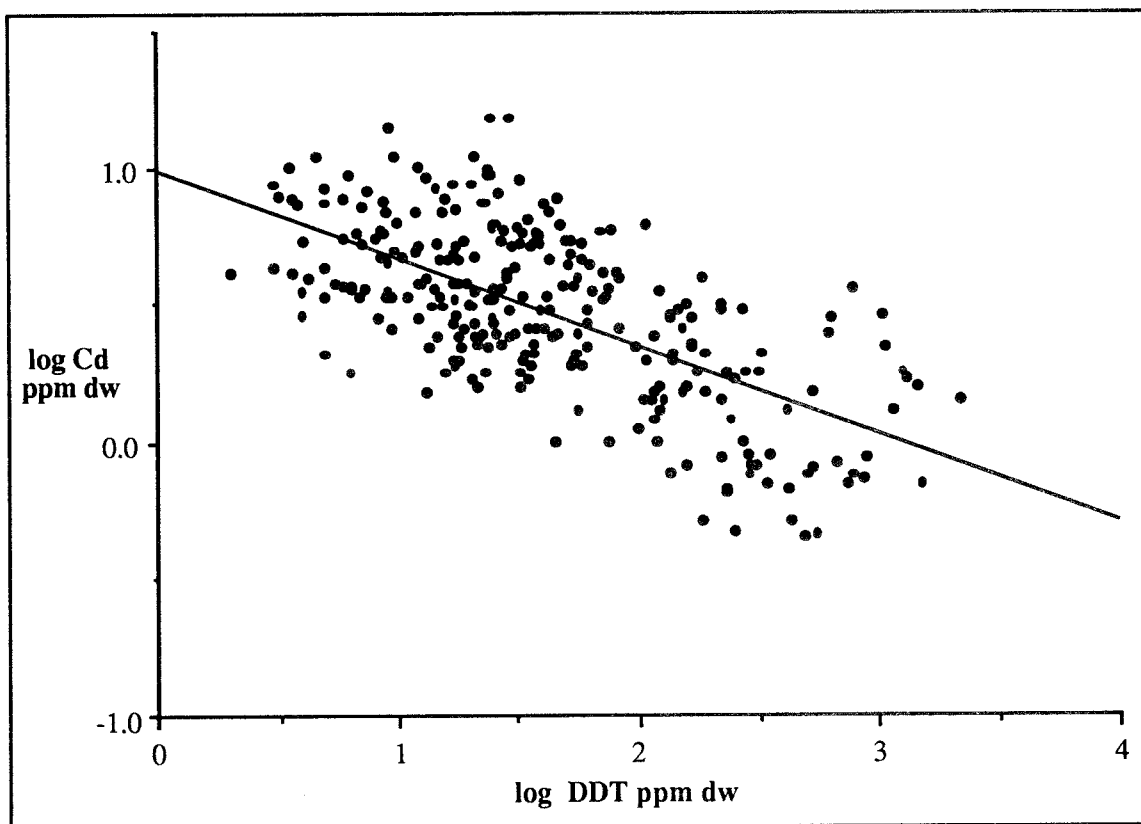
Figure 5.10. Relationship between cadmium and tDDT in tissues of M. californianus sampled by NOAA's NS&T program between 1986 and 1989 (NOAA, 1989 and unpublished data).

Cadmium levels in mussels nationwide vary greatly. Results of the first 4 years (1986-89) of NOAA's NS&T Mussel Watch Project indicate that mean levels of cadmium in *M. edulis* ranged from 0.2 to 15.467 ppm dw with an overall mean of 2.723 (median 2.267 ppm dw). Cadmium in *M. californianus* ranged from 0.477 to 14.667 ppm dw, with an overall mean value of 3.798 ppm dw (median 3.267 ppm dw).

Despite the large number of analyses of cadmium in mussels, there are few time-series collections for determining long-term trends in cadmium. Only two sites, Royal Palms State Park (near Whites Point) on the Palos Verdes Peninsula and a jetty at Oceanside, were occupied frequently over a 10-year period by the CMW. In both cases, no trends were apparent (p>>0.1) between fall 1977 and fall 1987 (Figure 5.14). The lack of a trend was consistent with long-term data from a third long-term CMW monitoring site at Montana de Oro State Park near San Luis Obispo in central California where cadmium in mussels was higher than at either Southern California Bight site, but also with no long-term trend (p>>0.1; Figure 5.14). The data from the Montana de Oro site are intriguing in that higher frequency sampling (quarterly) during 1983-85 revealed fourfold variations over short-perm periods (Figure 5.14). A fourfold inter-monthly variation (4 to 16 ppm dw) of cadmium was also observed in *M. californianus* from Bodega Head (northern California) between 1976 and 1978 (Goldberg *et al.*, 1978). However, in contrast to the southern California data, our analysis of Bodega Head data suggest the possibility of a long-term increase from about 8 ppm dw in the winter of 1976 to about 14 ppm dw in the fall of 1978 (p = 0.02).

The NOAA NS&T Mussel Watch Project has seen increases of cadmium in mussels from Palos Verdes and at the Los Angeles-Long Beach harbors breakwater since 1986 (Figure 5.15). Levels of cadmium in mussels from all other sites in southern California did not change between 1986 and 1988 (NOAA, 1989).

18.0

7.23
1.90
3.61

4.76

= 10 ppm dw

M. edulis

100 m

U.S.A.

Mexico
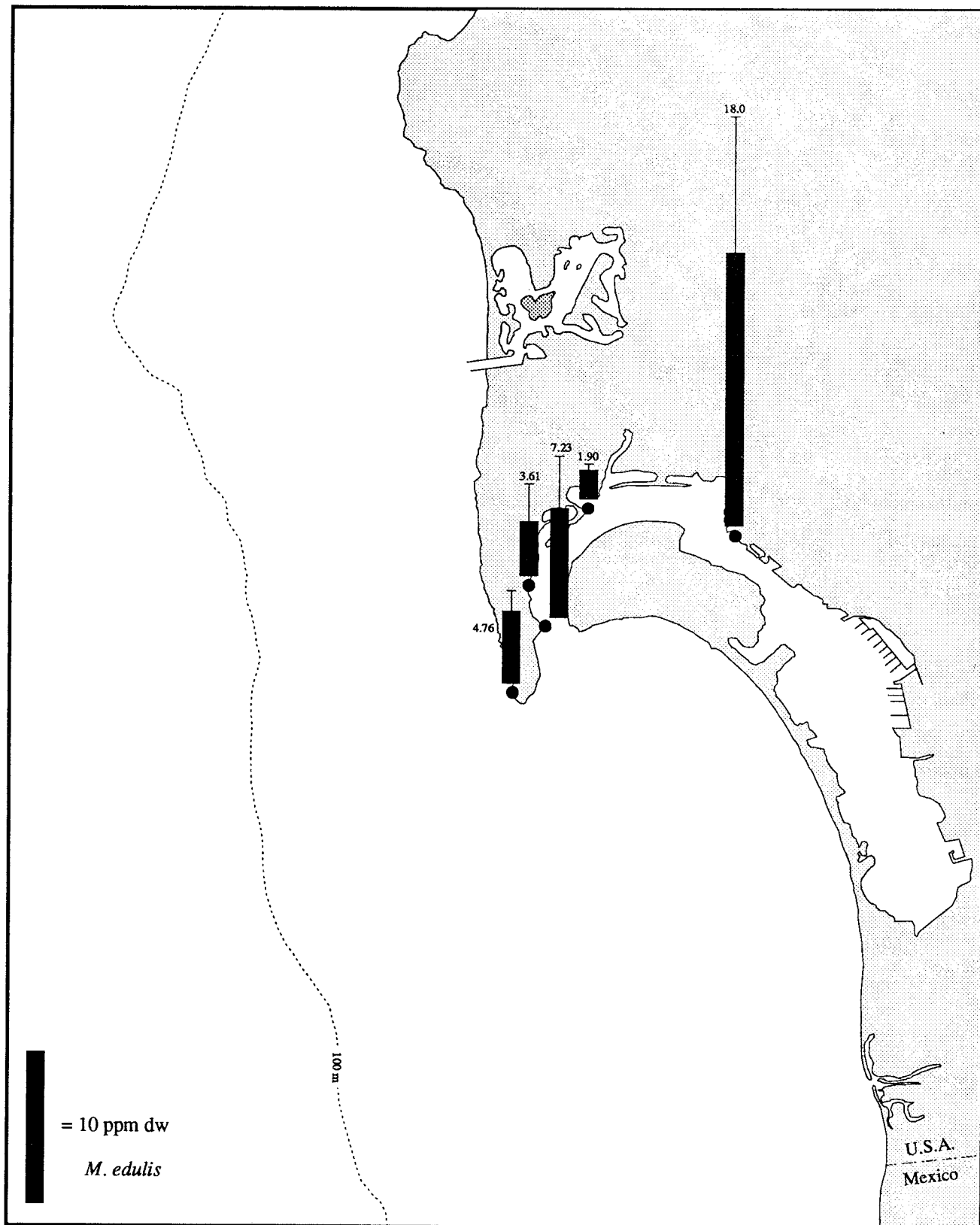
Figure 5.11. Cadmium in digestive gland tissue of mussels collected in 1974 in San Diego Harbor. Source: Young, unpublished data.
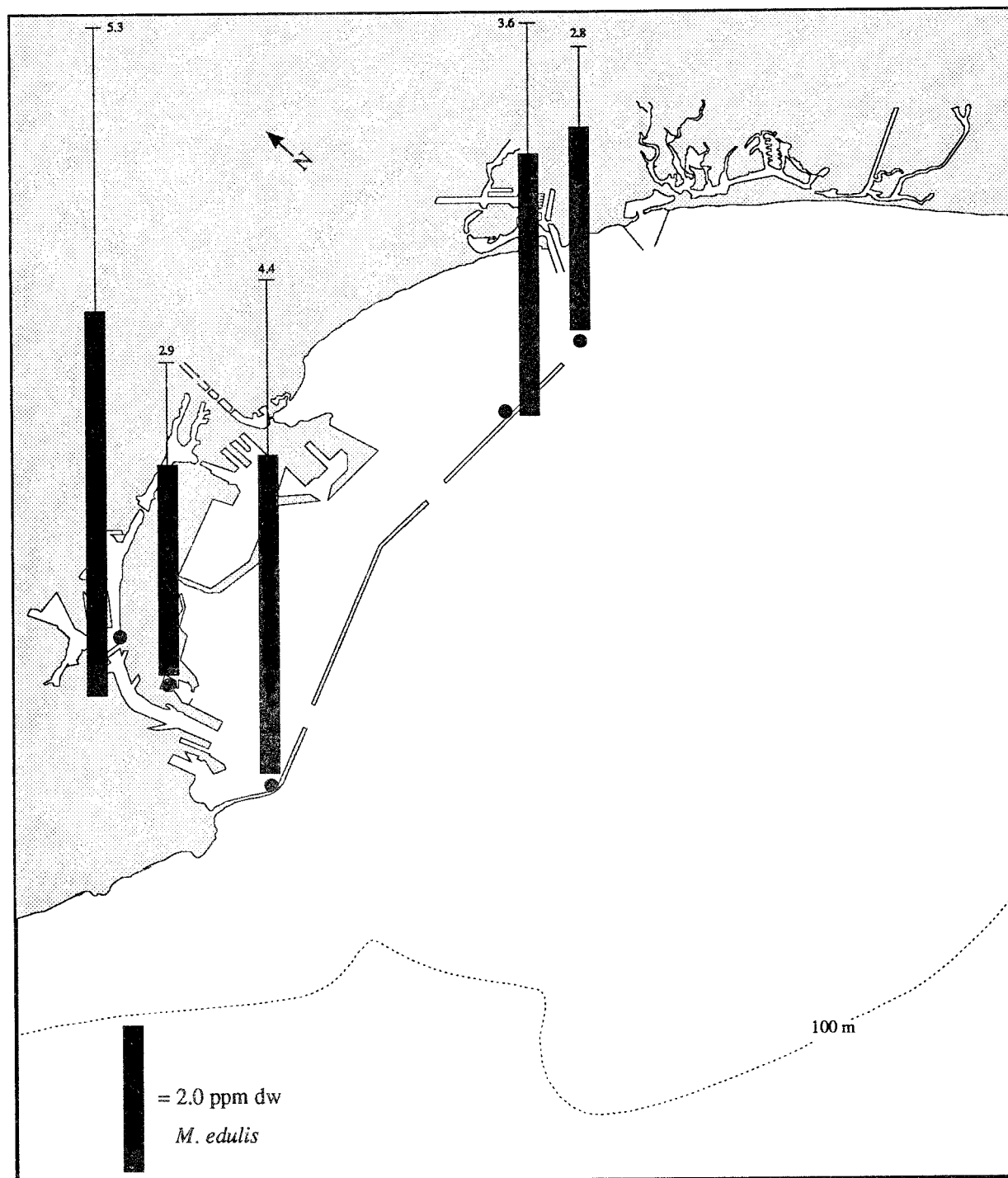
Figure 5.12. Cadmium in digestive gland of bay mussels sampled in San Pedro Bay in 1974. Error bars are 95% confidence intervals. Source: Alexander and Young, 1976.
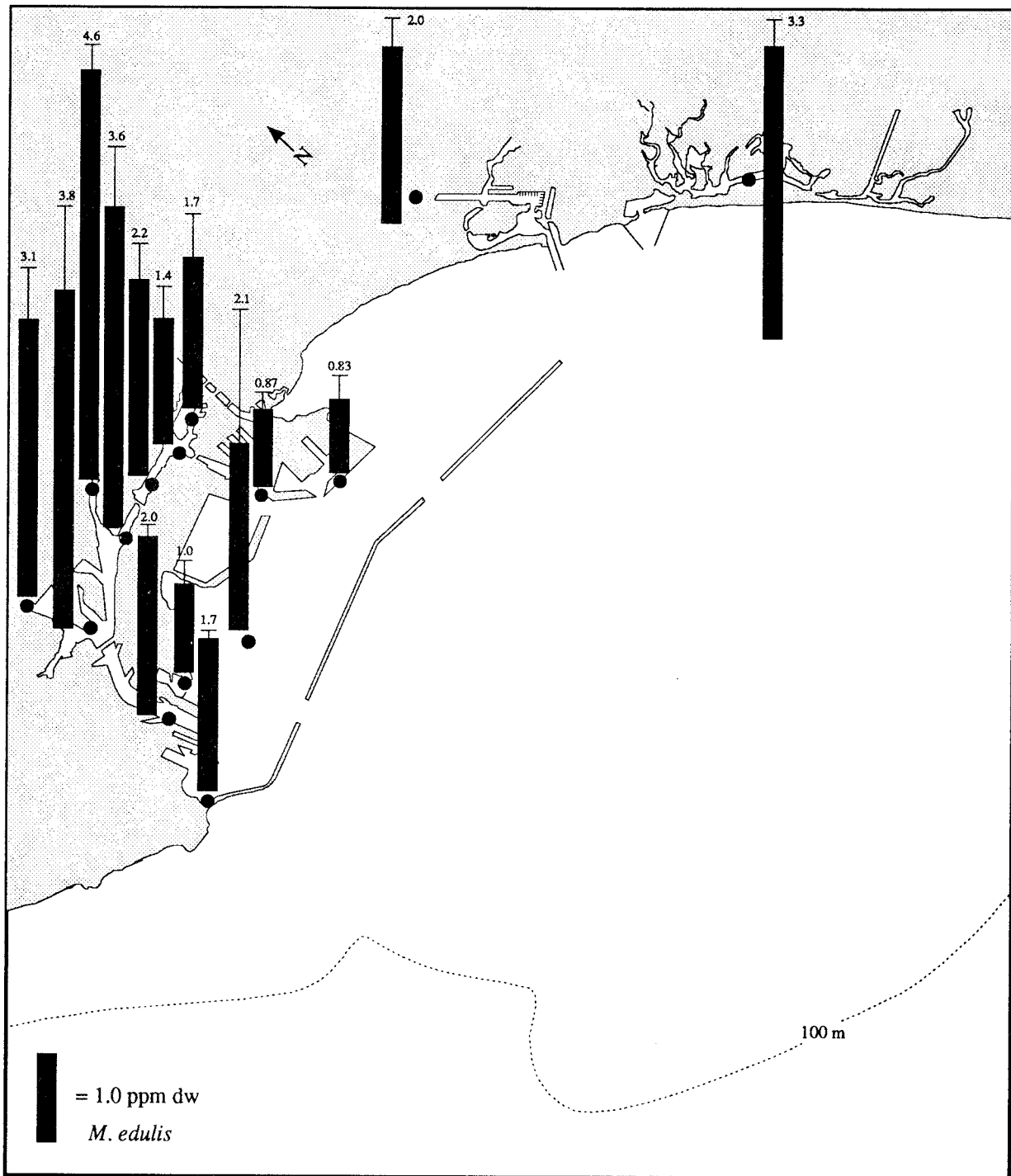
Figure 5.13. Cadmium in whole soft body tissue, less gonads, of bay mussels sampled in San Pedro Bay in 1982. Source: Phillips, 1988.

In summary, it appears that there have been two distributional patterns of cadmium concentrations in mussels of the Southern California Bight. Higher contamination in *M. californianus* in the restricted bay waters of San Diego, Los Angeles-Long Beach harbors and higher levels in those from offshore islands than those from mainland sites. Where time-series measurements have been made (Oceanside and Palos Verdes), there is no evidence of a long-term rise or decline, but seasonal fourfold variations are apparent.

CADMIUM IN FISH AND OTHER SPECIES

Cadmium has been measured in tissues of at least 30 species of macroinvertebrates and fish including 4 species of mollusks (other than mussels), 3 crustaceans, 17 fish, and 4 sharks. Concentrations in other than liver tissues have ranged from below detection (less than 0.001 ppm ww) in muscle of many kinds of fish to 1.55 ppm ww in samples of whole zooplankton collected in 1980 off Point Dume (Table 5.5). Concentrations in fish liver were higher, ranging from 0.008 ppm ww in Dover sole collected off Whites Point on the Palos Verdes Peninsula in 1971 (de Goeij and Guinn, 1972b) to 4.34 ppm ww in a composite of barred sand bass collected off Dana Point in 1984 (NOAA, 1987a and b).

The highest concentrations in muscle tissue sampled between 1975 and 1980 occurred in market squid from Santa Catalina Island (0.39 to 0.66 ppm ww) and in purple-hinge scallops from several sites (0.27 to 1.28 ppm ww; Table 5.4). Concentrations were intermediate (0.01 to 0.4 ppm ww) in muscle tissue of pelagic fish (northern anchovy, Pacific sardine, Pacific mackerel, swordfish (*Xiphius gladius*), and mako shark) and in black abalone from several intertidal sites. Lowest concentrations (less than 0.001 to 0.03) occurred in muscle tissue of a variety of nearshore and bottomfish including Dover sole, Pacific hake (*Merlussius productus*), Pacific sanddab, spotted sand bass (*Paralabrax maculatofasciatus*), striped bass, striped mullet (*Mugil cephalsu*), top smelt (*Atherinops affinis*), and white croaker and yellowfin croaker (*Umbrina roncador*) (Table 5.4).

Based on data shown in Table 5.5, Young (1988) concluded that cadmium does not appear to undergo biomagnification in onshore or coastal food webs of the Bight, and may decrease with trophic level.

Cadmium concentrations in muscle of sportfish caught in 1975-77 near the cadmium-enriched sediment field off the Palos Verdes Peninsula were not significantly higher than levels measured in island and coastal control specimens (Young *et al.*, 1978; Young *et al.*, 1981a; Table 5.6). However, the muscle tissues of rock scallops (*Hinnites multirugosus*) and edible portions of California spiny lobster collected at Palos Verdes concentrated cadmium 2 to 3 times above island or coastal background levels (Young *et al.*, 1978; Young *et al.*, 1981a; Young and Jan, 1979; Table 5.6). In contrast, cadmium concentrations were slightly, but not significantly, lower than at reference sites in two other tissues of rock scallops (digestive gland and gonad; Young and Jan, 1979). An inverse relation between tissue and sediment cadmium in Santa Monica Bay and off Palos Verdes was also demonstrated in four of five species of benthic fishes and macroinvertebrates sampled in 1983 by Brown *et al.*, (1984).

Mean cadmium concentrations in livers of Dover sole measured in 1971-72 by de Goeij *et al.* (1974) and de Goeij and Guinn (1972a and b) ranged from 0.08 ppm ww at two Palos Verdes sites to 3.3 ppm at a nearby site in Redondo Canyon (Figure 5.16). De Goeij *et al.* (1974) reported strong, significant evidence of cadmium depletion in livers of Dover sole from Palos Verdes compared to more distant and reference sites. For example, some mean concentrations at sites at Palos Verdes were 2 to 10 times lower than comparable samples from Santa Catalina Island (Figure 5.16). However, inspection of the original data indicates their analysis excluded two anomalously high concentrations (6.3 and 6.8 ppm ww) from southern Santa Monica Bay coastal sites.

Table 5.5. Cadmium concentrations (ppm ww) in edible tissues of marine organisms from the Southern California Bight.

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	Data Source
Kelp	Los Angeles Harbor	1980	5	0.126	0.123	0.113	0.141	0.011	Young and Mearns, 1980
Black Abalone	Palos Verdes	1975-77	3	0.047	0.041	0.034	0.067	0.017	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.028	0.028	0.027	0.029	0.001	Young et al., 1978
Gaper Clams	Los Angeles Harbor	1980	5	0.036	0.022	0.016	0.093	0.032	Young and Mearns, 1980
Market Squid	Coastal	1979-80	3	0.500	0.431	0.394	0.664	0.146	Schafer et al., 1982
Purple-hinge Scallop	Palos Verdes	1975-77	8	0.901	0.803	0.545	1.280	0.262	Young et al., 1978
	Santa Barbara	1975-77	2	0.398	0.398	0.358	0.437	0.056	Young et al., 1978
	Santa Catalina Island	1975-77	4	0.313	0.294	0.272	0.390	0.053	Young et al., 1978
Mysids (whole)	Palos Verdes	1980	7	0.085	0.054	0.018	0.161	0.060	Schafer et al., 1982
Zooplankton (whole)	Coastal	1979-80	5	0.830	0.860	0.063	1.550	0.544	Schafer et al., 1982
California Spiny Lobster	Palos Verdes	1975-77	3	0.019	0.019	<0.002	0.037	0.018	Young et al., 1978
	San Diego	1975-77	3	0.009	<0.002	<0.002	0.025	0.014	Young et al., 1978
	Santa Catalina Island	1975-77	3	<0.002	<0.002	<0.002	<0.002	<0.001	Young et al., 1978
Ridgeback Prawn	Palos Verdes	1980	5	0.012	0.013	0.004	0.021	0.006	Schafer et al., 1982
	Palos Verdes	1975-77	3	0.033	0.032	0.022	0.046	0.012	Young et al., 1978
	Orange County	1975-77	3	0.064	0.058	0.055	0.080	0.014	Young et al., 1978
	Dana Point	1975-77	3	0.004	0.004	<0.003	0.007	0.003	Young et al., 1978
Yellow Crab	Palos Verdes	1975-77	3	0.006	0.004	0.002	0.012	0.005	Young et al., 1978
	Dana Point	1975-77	3	0.011	0.010	0.010	0.012	0.001	Young et al., 1978
Bocaccio	Palos Verdes	1975-77	3	<0.002	<0.002	<0.002	<0.002	-	Young et al., 1978
	Orange County	1975-77	3	<0.001	<0.001	<0.001	<0.001	-	Young et al., 1978
	San Clemente Island	1975-77	3	<0.002	<0.002	<0.002	<0.002	0.001	Young et al., 1978
California Halibut	Los Angeles Harbor	1980	4	0.002	0.002	<0.001	0.003	0.001	Young and Mearns, 1980
	Palos Verdes	1975-77	2	<0.002	<0.002	<0.002	<0.002	-	Young et al., 1978
	Oxnard	1975-77	2	0.001	<0.002	<0.002	<0.003	<0.001	Young et al., 1978
California Scorpionfish	Palos Verdes	1980	4	0.006	0.005	0.001	0.016	0.007	Schafer et al., 1982
	Palos Verdes	1975-77	3	0.024	0.004	<0.001	0.067	0.037	Young et al., 1978
	Orange County	1975-77	3	0.002	0.001	<0.001	0.003	0.001	Young et al., 1978
	Dana Point	1975-77	3	0.002	<0.002	<0.002	0.003	<0.001	Young et al., 1978
Dover Sole	Palos Verdes	1980	5	0.006	0.006	0.005	0.008	0.001	Schafer et al., 1982
Northern Anchovy	Los Angeles Harbor	1980	5	0.009	0.003	<0.001	0.030	0.013	Young and Mearns, 1980
	Coastal	1979-80	5	0.172	0.164	0.038	0.379	0.128	Schafer et al., 1982
Pacific Hake	Coastal	1979-80	5	0.003	0.002	<0.001	0.007	0.003	Schafer et al., 1982
Pacific Mackerel	Coastal	1979-80	5	0.059	0.061	0.001	0.101	0.037	Schafer et al., 1982
Pacific Sanddab	Palos Verdes	1975-77	3	0.002	0.003	0.001	0.003	0.001	Young et al., 1978
	Orange County	1975-77	3	0.004	0.003	0.002	0.006	0.002	Young et al., 1978
	Dana Point	1975-77	3	0.002	<0.002	<0.002	0.003	0.001	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.005	0.004	0.002	0.009	0.004	Young et al., 1978
Pacific Sardine	Coastal	1979-80	5	0.021	0.017	0.002	0.036	0.015	Schafer et al., 1982
Pcific Bonito	Coastal	1979-80	5	0.010	0.010	0.001	0.019	0.007	Schafer et al., 1982
Spotted Sand Bass	Newport Bay	1978	3	0.003	0.003	0.002	0.005	0.002	MBC and SCCWRP, 1980
Striped Bass	Newport Bay	1978	3	0.003	0.003	0.002	0.003	0.001	MBC and SCCWRP, 1980
Striped Mullet (adult)	Newport Bay	1978	3	0.020	0.020	0.001	0.029	0.010	MBC and SCCWRP, 1980
Striped Mullet (juvenile)	Newport Bay	1978	3	0.001	0.001	0.001	0.002	0.001	MBC and SCCWRP, 1980
Swordfish	Coastal	1979-80	5	0.078	0.079	0.030	0.117	0.034	Schafer et al., 1982
Topsmelt	Newport Bay	1978	3	0.005	0.002	0.001	0.011	0.010	MBC and SCCWRP, 1980
White Croaker	Los Angeles Harbor	1980	5	0.042	0.004	<0.001	0.200	0.088	Young and Mearns, 1980
	Palos Verdes	1980	5	0.001	0.001	0.001	0.005	0.002	Shafer et al., 1982
	Palos Verdes	1975-77	3	<0.001	<0.001	<0.001	<0.001	-	Young et al., 1978
	Orange County	1975-77	3	0.001	0.001	<0.001	0.002	0.001	Young et al., 1978
	Dana Point	1975-77	3	0.002	<0.002	<0.001	0.003	0.001	Young et al., 1978
Yellowfin Croaker	Newport Bay	1978	3	0.003	0.002	0.002	0.004	0.001	MBC and SCCWRP, 1980
Mako Shark	Coastal	1979-80	5	0.043	0.029	0.010	0.099	0.034	Schafer et al., 1982
Spiny Dogfish	Palos Verdes	1980	5	0.018	0.012	0.006	0.037	0.012	Schafer et al., 1982
Thresher Shark	Coastal	1979-80	5	0.010	0.009	0.001	0.029	0.009	Schafer et al., 1982
White Shark	Coastal	1979-80	3	0.002	0.002	0.001	0.004	0.001	Schafer et al., 1982
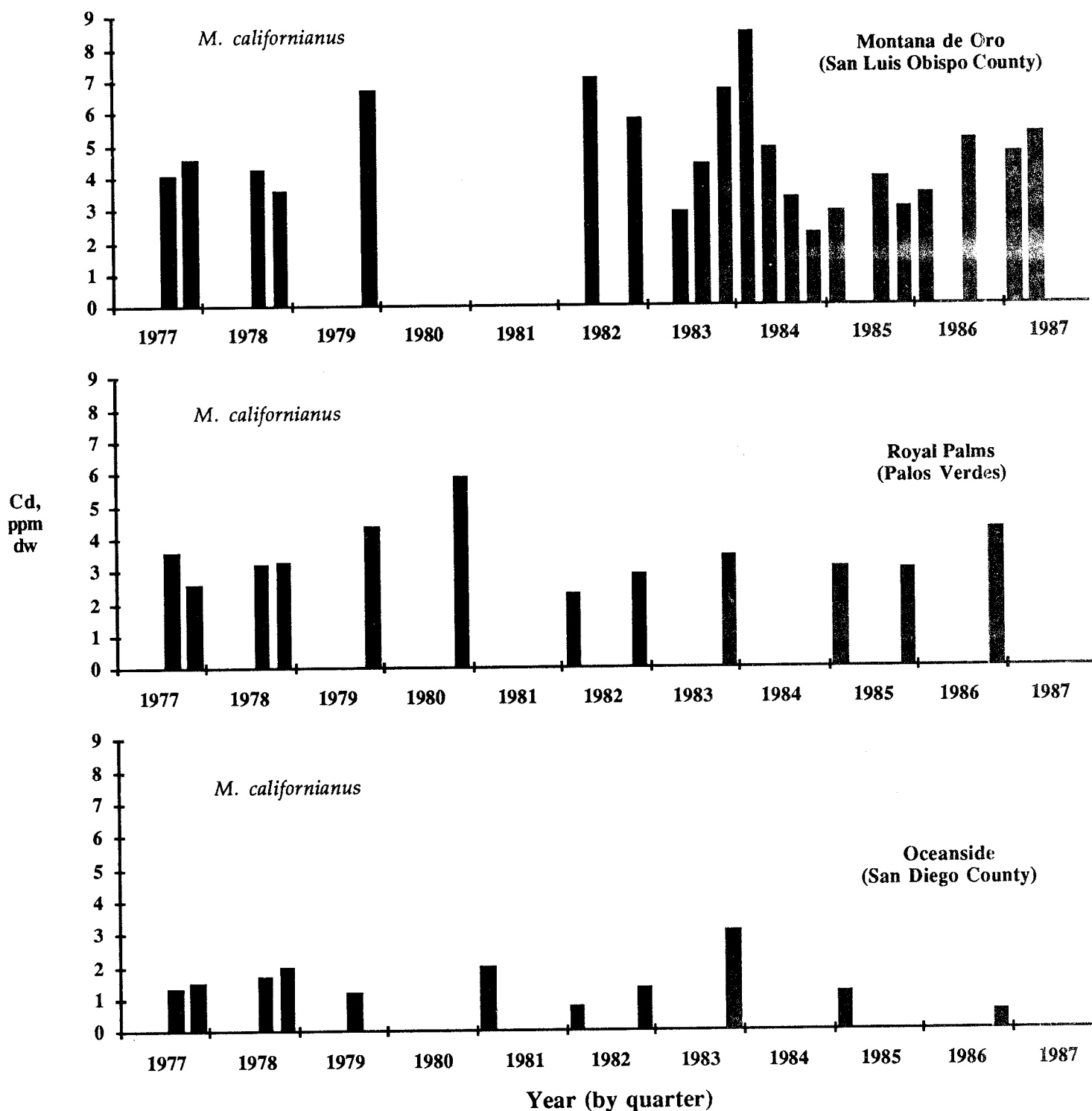
Figure 5.14. Long-term (1977-87) trends of cadmium in mussels from three CMW Program sites: Montana de Oro State Park, San Luis Obispo County; Royal Palms State Park, Palos Verdes Peninsula, Los Angeles County; and Oceanside jetty, San Diego County. Source: Phillips, 1988.
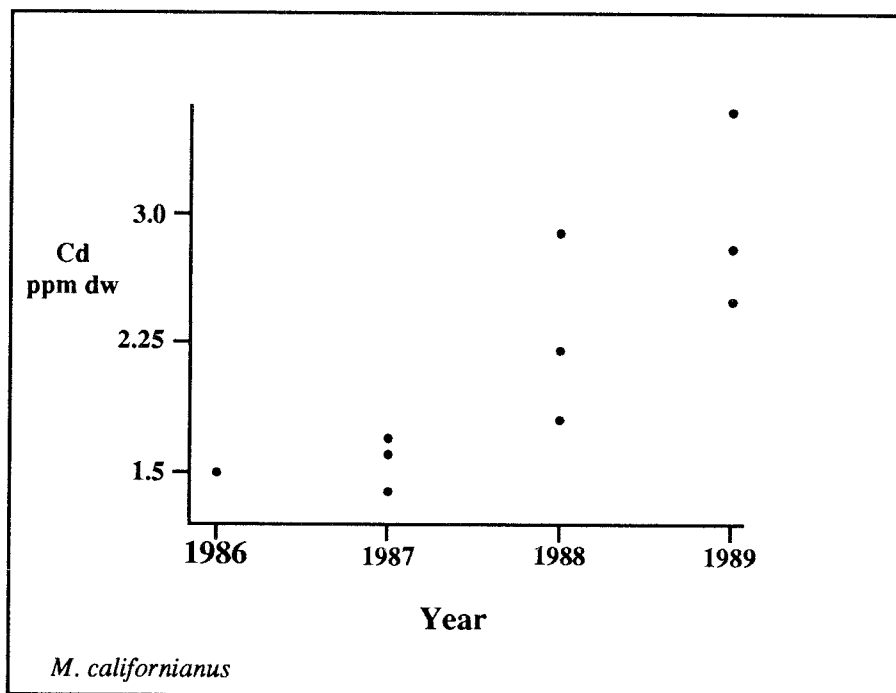
Figure 5.15 Cadmium sampled at Royal Palms by NOAA's NS&T Program (NOAA, 1989 and unpublished data).

Cadmium concentrations in muscle of sportfish caught in 1975-77 near the cadmium-enriched sediment field off the Palos Verdes Peninsula were not significantly higher than levels measured in island and coastal control specimens (Young et al., 1978; Young et al., 1981a; Table 5.6). However, the muscle tissues of rock scallops (*Hinnites multirugosus*) and edible portions of California spiny lobster collected at Palos Verdes concentrated cadmium 2 to 3 times above island or coastal background levels (Young et al., 1978; Young et al., 1981a; Young and Jan, 1979; Table 5.6). In contrast, cadmium concentrations were slightly, but not significantly, lower than at reference sites in two other tissues of rock scallops (digestive gland and gonad; Young and Jan, 1979). An inverse relation between tissue and sediment cadmium in Santa Monica Bay and off Palos Verdes was also demonstrated in four of five species of benthic fishes and macroinvertebrates sampled in 1983 by Brown et al., (1984).

Mean cadmium concentrations in livers of Dover sole measured in 1971-72 by de Goeij et al. (1974) and de Goeij and Guinn (1972a and b) ranged from 0.08 ppm ww at two Palos Verdes sites to 3.3 ppm at a nearby site in Redondo Canyon (Figure 5.16). De Goeij et al. (1974) reported strong, significant evidence of cadmium depletion in livers of Dover sole from Palos Verdes compared to more distant and reference sites. For example, some mean concentrations at sites at Palos Verdes were 2 to 10 times lower than comparable samples from Santa Catalina Island (Figure 5.16). However, inspection of the original data indicates their analysis excluded two anomalously high concentrations (6.3 and 6.8 ppm ww) from southern Santa Monica Bay coastal sites.

Similar patterns may be discerned in livers of hornyhead turbot from four 1984 NOAA NS&T Benthic Surveillance sites (Figure 5.17). Fish from sites near Dana Point and in San Diego Bay (outside San Diego Harbor) had concentrations higher than those from Santa Monica Bay and San Pedro Canyon (where sediment levels were much higher). In two other species, barred sand bass and white croaker, cadmium concentrations were also higher at the Dana Point reference site than at urban sites (San Diego Harbor and Seal Beach, respectively; Figure 5.17). Curiously, cadmium concentrations were extremely high (100 to 200 ppm dw) in sea-skaters (*Halobates*) collected from the sea surface several thousand km offshore of San Diego (Cheng et al., 1976).

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Table 5.6. Mean levels of cadmium (ppm ww) and standard deviation in edible tissue composites of 10 popular seafood organisms collected 1975-78. Number of samples indicated in parentheses. Young *et al.*, 1978; Young *et al.*, 1981.

COMMON NAME	COASTAL SITES						ISLAND SITES		
	POINT DUME-OXNARD	PALOS VERDES	SAN PEDRO BAY	LAGUNA BEACH	DANA POINT	SAN DIEGO	SANTA BARBARA	SANTA CATALINA	SAN CLEMENTE
Black abalone	--	0.047 ±0.017 (3)	--	--	--	--	--	0.028 ±0.001 (3)	--
Purple-hinge scallop	--	0.901 ±0.262 (3)	--	--	--	--	0.348 ±0.056 (2)	0.313 ±0.053 (4)	--
Yellow crab	--	0.006 ±0.005 (3)	--	--	0 0.11 ±0.001 (3)	--	--	--	
Ridgeback prawn	--	0.033 ± 0.012 (3)	--	--	0.004 ±0.003 (3)	--	--	--	
California spiny lobster		0 019 ±0.018 (3)	--	--	--	0.009 ±0.019 (3)	--	0.001 ±0.000 (3)	--
Pacific sanddab	--	0.002 ±0.001 (3)	0.004 ±0.002 (3)	--	0.002 ±0.001 (3)	--	0.005 ±0.004 (3)	--	
California halibut	0.001 ±0.000 (2)	0.001 ±0.000 (2)	--	--	--	--	--	--	
White croaker	--	0.001 ±0.000 (3)	0.001 ±0.001 (3)	--	0.002 ±0.001 (3)	--	--	.	--
Bocacio	--	0.001 ±0.000 (3)	0.001 ±0.001 (3)	--	--	--			0.001 ±0.001 (3)
Scorpionfish		0.024 ±0.037 (3)	0.002 ±0.001 (3)	--	0.001 ±0.000 (3)	--		--	
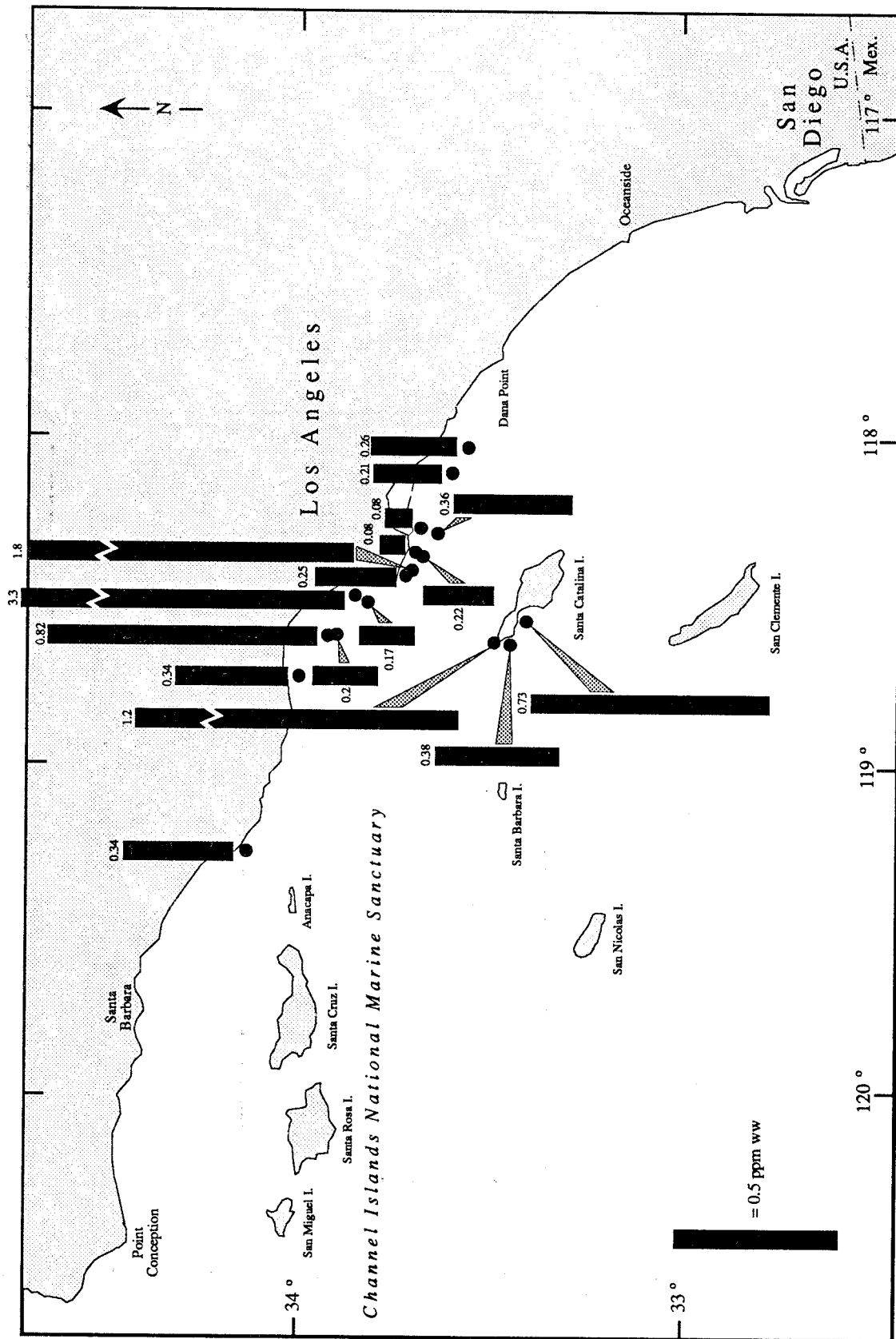
Figure 5.16. Cadmium concentrations in liver tissue of Dover sole collected in the Southern California Bight in 1971-72. Source: de Goeij and Guinn (1972 a; b).
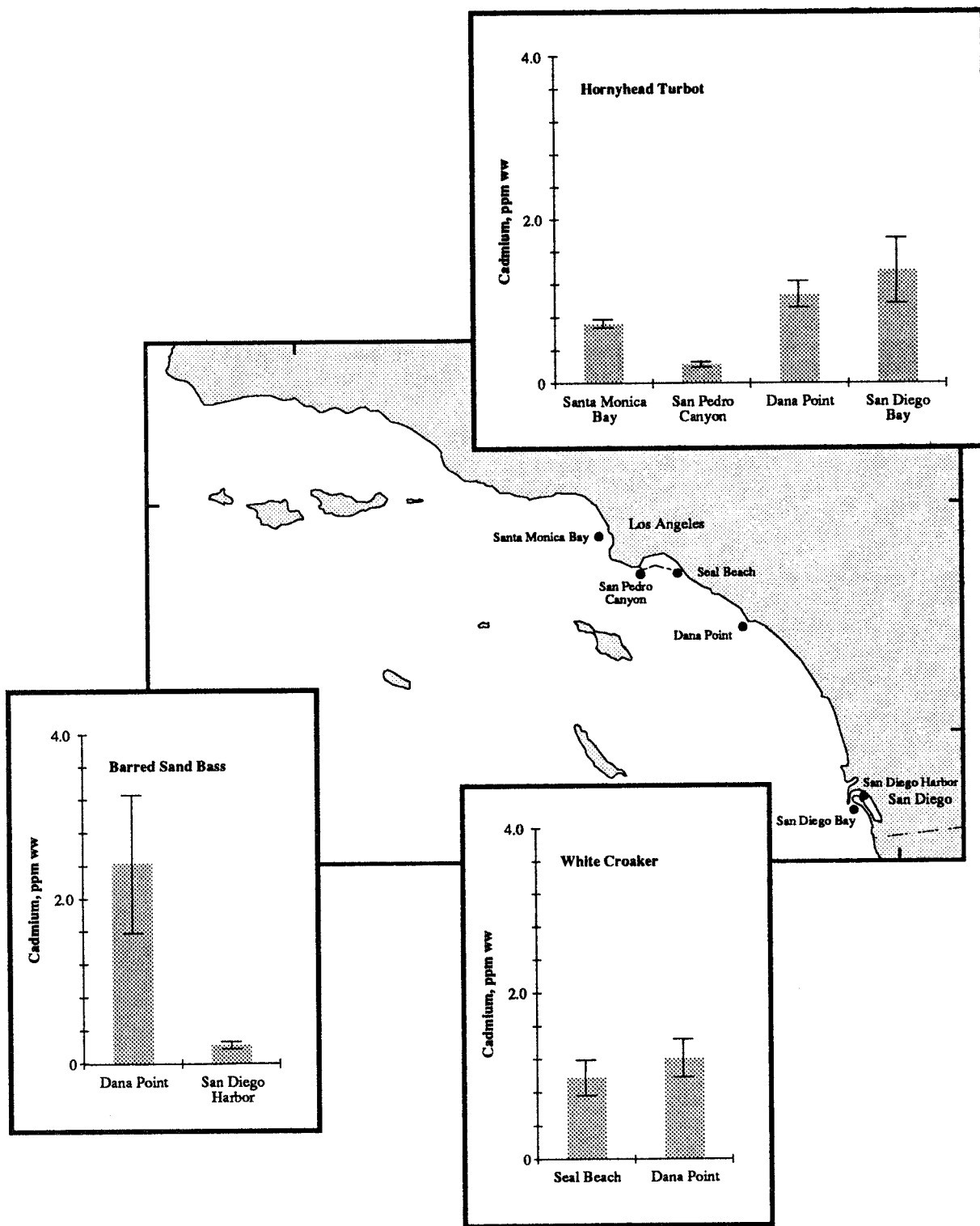
Figure 5.17. Concentrations of cadmium measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

The possibility exists that cadmium is highly variable seasonally and interannually in livers of bottom fish. For example, quarterly monitoring by CSDOC in the area of the Orange County outfall off Huntington Beach (CSDOC, 1986) resulted in median cadmium levels in hornyhead turbot that rose from 0.6 to 3.9 ppm ww between summer and fall of 1984, then declined to 1.6 to 1.8 ppm ww during the winter and spring of 1985. By summer 1987, (CSDOC, 1988) the median level was 0.4. During this period, cadmium emissions (from the outfall) and sediment levels were decreasing. These variations agree with those in white croaker as measured by SCCWRP from monthly sampling at Dana Point and Palos Verdes, where liver cadmium concentrations varied nearly 10-fold during the year (unpublished data).

There is no seafood criteria or guideline for cadmium in the United States. The median of five international criteria or standards (Nauen, 1983) is 1.0 ppm ww (range 0.1 to 2.0). None of the median values for edible tissues reported in Table 5.4 exceed this international median standard, but the 1975-77 scallops from Palos Verdes approached it (0.803 ppm ww). Squid, kelp, zooplankton, all scallops, and northern anchovy from the open coastal zone exceeded the minimum criteria of 0.1 ppm ww. Likewise, most liver samples exceeded this value and many exceeded the 1.0 ppm ww median.

SUMMARY AND CONCLUSIONS

Cadmium has been frequently measured in sediments, mussels, and tissues of fish from the Southern California Bight. Compilation of these data suggest that its distribution in sediments is a function of proximity to point sources, but its distribution in marine organisms may be influenced by other factors such as upwelling (Martin et al., 1981). Existing data do not support Aylett's (1979) claim that cadmium undergoes bioconcentration in food webs, at least in the Southern California Bight.

In the past, waste water and other anthropogenic inputs of cadmium have led to extensive and possibly toxic cadmium contamination of coastal and harbor sediments and localized contamination in tissues of several inshore invertebrates at the Palos Verdes Peninsula. Recently (1980-87), sediment concentrations at Palos Verdes and in Los Angeles-Long Beach harbors have declined to levels below concentrations believed to be toxic. Cadmium was not elevated in mussels and most other species sampled near a major cadmium source (the JWPCP sewage outfalls at Palos Verdes), but was elevated in abalone, scallops, and scorpionfish (*Scorpaena guttata*) during 1975-77. It is not known if cadmium has decreased in these species since then. Sediment contamination has occurred in portions of inner Los Angeles-Long Beach harbors and in very localized areas around sewage discharge sites. Despite these contamination epicenters, existing data indicate that cadmium in waste water and sediments has not caused high levels of contamination of most fish and macroinvertebrates, even in close proximity to areas with elevated sediment concentrations. However, *M. edulis* in inner portions of San Diego, Los Angeles, and Long Beach harbors did yield higher tissue cadmium concentrations than those from the outer areas of the harbors.

There is strong evidence that cadmium has not undergone bioconcentration or biomagnification in coastal food webs of the Bight. Indeed, there is evidence that some fishes and invertebrates from urban areas may have less cadmium than the same species from uncontaminated areas. De Goeij et al. (1974) first pointed out the possibility of cadmium depressions in fish exposed to highly contaminated sediments. Young and Jan (1979) suggested the depression might be an effect of the high chlorinated hydrocarbon loads carried by these fish and cited an experimental study by Nimmo and Bahner (1976) that confirmed an antagonistic interaction between cadmium and the organochlorine pesticide methoxychlor. Brown et al. (1987) postulated a mechanism for this interaction whereby chlorinated hydrocarbon metabolites compete with cadmium and other metals for glutathione binding sites. Thus, the extent to which cadmium is lower in fish (and in some tissues of some invertebrates) from outfall areas may be a measure of the extent of chlorinated hydrocarbon contamination.

In addition, a second, large-scale mechanism--possibly upwelling--seems to be operating to influence cadmium distribution in marine organisms of the Bight. Observing the negative correlation between cadmium body burdens in *M. californianus* and proximity to urban areas, Stephenson et al. (1979a and b) speculated that coastal upwelling is a significant source of cadmium in waters of the Southern California Bight. This argument is strengthened by investigations which have demonstrated that cadmium concentrations off the coast of California are depleted in surface waters and enriched at mid-depth (Martin et al., 1976).

INFORMATION NEEDS

Ambient monitoring is needed to determine trends of cadmium contamination in mussels from inner portions of Los Angeles-Long Beach and San Diego harbors and in abalone, scallops, and scorpionfish from Palos Verdes (and respective reference sites) to confirm that documented waste reductions have resulted in a return to background levels in these particular species and areas. Beyond that, pollution abatement activities may actually result in increased levels of cadmium in livers of bottomfish in several areas, a hypothesis testable through additional monitoring at discharge and remote reference sites. Finally, ambient monitoring elsewhere should be done in such a way as to accommodate seasonal and interannual variability due to upwelling of cadmium-rich deep water. The Orange County and other existing data sets should be explored in more detail for unusual spatial and temporal patterns.

CHAPTER 6

CHROMIUM

Chromium is used in a number of industrial applications, chiefly metallurgical and chemical. It is an important component of stainless steel and also is used for production of pigments, tanned leather, wood preservatives, and anticorrosives (Goyer, 1986). Primary sources of chromium to the aquatic environment are metal finishing industries and municipal waste treatment plants (Eisler, 1986b).

Chromium is common in the earth's crust. Sedimentary rock contains up to 160 ppm chromium (Purves, 1985). It ranks fourth of the 29 elements of biological importance and occurs in oxidation states from Cr^{2+} to Cr^{6+}. However, only the trivalent and hexavalent forms are biologically important (Goyer, 1986). According to a synopsis of research results assembled by Eisler (1986b), the +3 form of chromium forms the basis of a number of compounds that function in glucose, lipid, and protein metabolism, thus making chromium an essential element in mammals. The +6 form of chromium is considered to be more toxic than the +3 form because of its high oxidizing potential and ability to cross cellular membranes. Jop et al. (1987) cited results from several studies that indicate that the pH of the aqueous medium to which organisms are exposed can markedly affect uptake and accumulation of hexavalent chromium. Jop et al. also found that laboratory toxicity of hexavalent chromium was not highly pH dependent, although they noted that other studies had produced contrary results.

Eisler (1986b) stated that little is known about the relation between concentrations of total chromium in the environment and biological effects on resident organisms. While inorganic trivalent chromium is not believed to bioaccumulate to a great extent, Eisler noted that the behavior of organic chromium species in biological systems has not been well described. However, bivalves have been shown to accumulate chromium from contaminated water and sediments, with salinity of the medium, weight of the organism, and dissolved chromium concentration affecting ultimate tissue concentrations (Eisler, 1986b).

In all of the studies forming the basis for discussion here, the measurements of chromium are expressed as total chromium, as opposed to the trivalent or hexavalent forms of the element. Jan and Young (1976) analyzed oxidation states of chromium in both relatively clean coastal seawater and in municipal waste discharges. They found that while most (58 to 67 percent) of the dissolved chromium in seawater was in the +6 state, only 1 to 3 percent of that in wastewater was hexavalent. The majority of chromium in wastewater (97 to 99%) was in the relatively non-toxic trivalent form (Jan and Young, 1976). They determined that the particulate fraction of total chromium varied considerably from effluent to effluent, depending upon specific treatment plant and degree of treatment.

Unfortunately, the oxidation state(s) (and toxicity) of chromium in marine sediments is not known. However, if it is largely in the reduced (Cr^{+3}) state, such as a hydroxide, (possible in sediments contaminated by sewage) then there is data that would suggest that the excess chromium is not toxic at any concentration. Marine polychaetes (*Neanthes arenaceodentata*) suffered no mortality, reproduced successfully over several generations, and incurred no bioaccumulation in a pure trivalent chromium silt which precipitated from a nominal concentration of over 50,000 ppm Cr^{+3}. In contrast, exposure to concentrations of Cr^{+6} as low as 0.02 ppm did inhibit reproduction and resulted in bioaccumulation (Oshida 1976; 1977). These experiments and observations underscore the need to determine chromium oxidation states in sediments and interstitial waters. The significance of chromium concentrations found in resident biota is unknown and remains a topic for further study and analysis.

In 1971, sewage wastewaters were estimated to be the predominant anthropogenic source of chromium to the Southern California Bight, accounting for 649 of 703 mt of input (SCCWRP, 1973). Sewage inputs have since declined nearly tenfold to a total of 60 mt per year in 1987 (SCCWRP, 1988) making runoff a comparable source. Runoff from the Los Angeles River carried 6 mt in 1971-72, 67 mt in the highflow wet cycle of 1979-80, and 11 mt in 1985-86 (Schafer and Gossett, 1988).

CHROMIUM IN SEDIMENTS

Chromium has been one of the most frequently measured chemicals in shelf, basin, and bay sediments of the Southern California Bight (Table 6.1). It is likely that as a result of long-term compliance monitoring programs and extensive research surveys, there may exist over 10,000 sediment chromium measurements since early determinations by Galloway (1972a and b; 1979) at five outfall sites in 1970-71 (also see SCCWRP, 1973).

Depending upon the strength of extracting reagents employed, background concentrations of chromium on the mainland shelf have been reported to range from about 5 to 25 ppm dw (weak acid leachable) to about 40 ppm dw (43.5 as computed in Katz and Kaplan, 1981 for "strong acid" total chromium). Basin sediments were reported to contain higher concentrations (20 to 100 ppm dw) than shelf sediments (Katz and Kaplan, 1981). In samples collected off the relatively uncontaminated coast between Point Dume and Port Hueneme and over a depth range of 14 to 745 m, chromium concentration increased significantly ($p < .001$) with water depth, volatile solids, and clay content; and decreased significantly with increasing solids content (Hershelman et al., 1982). These "background" concentrations varied from about 10 to 20 ppm dw at 20 m to 60 to 90 ppm at more than 500 m (Hershelman et al. 1982). Word and Mearns (1979) estimated a coastal shelf "background" along the 60-m isobath at about 29 ppm dw. No comparable estimates have been made for bays or lagoons.

The overall mean level of chromium in sediments measured by NOAA's NS&T Program from all sites between 1984 and 1989 is considerably higher than the background concentrations calculated by other investigators. The overall mean level of chromium was 84.312 ppm dw, while the median value was 57.333 ppm dw.

In both the 1977 and 1985 control and reference surveys conducted by SCCWRP (Word and Mearns, 1979; Thompson et al., 1987), chromium concentrations at 60-m were low along most of the coast, showed a slight (2 to 3 times) rise across Santa Monica Bay and a major peak at Palos Verdes (Figures 6.1 and 6.2). A similar pattern, but with considerably lower peak concentrations, was apparent in the 1986 NOAA NS&T Mussel Watch sediment data (Figure 6.3). San Diego Harbor also had elevated chromium levels in sediment.

To compare areas, median values from the most recent survey in each area were isolated and ranked, identifying the Palos Verdes shelf (at 60 m) in 1985, San Diego Harbor in 1983, and Los Angeles-Long Beach harbors in 1978 as the three areas with highest levels of chromium (survey medians were 273, 113, and 87 ppm dw, respectively; Table 6.2). To gain some idea of excess above background, these median were compared to the 1977 60-m control survey background concentration of 29 ppm dw. This resulted in elevations of nearly 10 times background (9.4) along the Palos Verdes shelf 60-m isobath, and threefold or greater in San Diego Harbor (3.9) and Los Angeles-Long Beach harbors (3.0). However, sediments from a few areas contained less chromium than the 29 ppm dw reference value (Point Loma and Tijuana; Table 6.2). The extremely low concentrations in the Tijuana Estuary may indicate that reference or background levels in shallow bays, lagoons, and harbors should be considerably less than the coastal shelf reference of 29 ppm dw. Based on the Tijuana Estuary data, a bay-lagoon-harbor reference value of 6 ppm dw was used to compute a second set of elevation factors for the remaining bays and harbors. The effect of this was a re-ranking in which San Diego Harbor and Los Angeles-Long Beach harbors were most contaminated (18.8 and 14.5 times background, respectively), followed by the Palos Verdes shelf (9.4 times). In addition, this computation suggested that sediments in Marina del Rey, near Newport Bay shipyards, and in Upper Newport Bay contain more excess chromium (6.8, 5.2, and 4.8 times background) than do all remaining coastal and inshore sites including Santa Monica Bay (2.5 times background). The dilemma of what constitutes natural background levels is unresolved, but clearly a resolution is needed to help identify areas with true excess contamination.

Table 6.1. Mean, median, minimum, and maximum chromium concentrations in surface sediment from selected surveys, 1970-1985 in ppm dw.

SITE	Year	N	Mean	Median	Min	Max	SD	Source
Rural Coastal Shelf (60-m depth only):								
Santa Barbara shelf	1977	11	27.2	27	16	42	8.99	1
	1985	4	31.3	3.05	27	37	4.6	2
Port Hueneme to Point Dume	1977	4	25.5	24.5	165	37	10.6	1
	1980	11	36.5	37	24	50	9.2	3
	1985	2	30.5	30.5	21	40	13.4	2
Newport to Dana Point	1977	3	23	24	19	26	3.6	1
	1978	6	28.8	29	16	40	7.7	4
	1985	1	29 -	---	----	----	----	2
Outfall Areas:								
Oxnard shelf	1971[a]	4	44	37	33	70	17	9
Santa Monica Bay	1970[a]	24	111	110	34	220	43.2	9
	1977[b]	13	77.1	69	43	146	33.9	1
	1978[b]	31	113.1	90	34	627	103.7	4
	1985[b]	3	47.7	55.3	21.1	667	23.7	5
Palos Verdes shelf	1970[a]	22	287	235	43	860	203	9
	1977[b]	8	597	590	25	1317	486	1
	1978[b]	8	566	567	104	1042	287	4
	1985[b]	20	332	273	76.1	804	219	6
Orange County shelf	1970[a]	13	44.8	42	24	68	12.9	9
	1977[b]	11	38.5	37	22	63	10.2	1
	1978[b]	12	32.9	31	20	51	7.8	4
	1985[b]	9	23.6	23.6	18.4	36.9	5.46	7
Point Loma shelf	1970[a]	6	59	43	38	140	39.9	9
	1977[b]	7	22.6	23	18	28	3.36	1
	1985[b]	7	21.3	20	18	32	4.8	8
Bays and Harbors:								
Marina del Rey[a]	1977	11	91.5	94.1	27.1	129	29.7	10
	1978	11	53.8	55.3	29.3	82.1	15.3	10
	1984	12	56.5	50.1	33.7	83.3	16.7	11
	1985	12	43.4	46.5	5.9	72.1	21.4	12
	1987	13	41.1	41	6.5	70.4	20.2	13
Los Angeles-Long Beach harbors [a]	1973	31	96.7	79.8	14.0	359	77.7	14
	1978	3	11.7	87.4	16	221	47.7	15
Lower Newport Bay	1971	7	21	16	12	31	8.3	19
Upper Newport Bay[a]	1971	3	16.3	21	2	26	12.7	19
	1975-76	---	78	--	--	--	--	16
	1980	8	26.2	29.3	14.7	30.9		17
San Diego Harbor[a]	1974	11	56.5	54.1	22	97	21.8	19
	1983	20	170	112.5	54	1300		18
Newport Shipyards	1972	9	119	103	45	232	54	20
	1981	8	34.5	34	22	52	34	20
	1986	6	25.2	31	9	36	10.3	20
Tijuana Estuary, mouth	1988	5	2.67	2.83	2.25	2.95	0.29	21
Tijuana Estuary, north	1988	14	6.54	6.08	0.43	16.5	3.79	21
Tijuana Estuary, south	1988	26	12.85	9.03	2.32	32.04	9.66	21
OVERALL					0.43	1314		

[a] all depths; [b] 60-m only

1 Word and Mearns,1979	8 City of San Diego, original data	15 Soule and Oguri, 1980a
2 Thompson *et al.*, 1987	9 SCCWRP, 1973; Galloway, 1972a&b)	16 Christiansen *et al.*,, 1978
3. Hershelman *et al.*, 1982	10 Soule and Oguri, 1980b	17 MBC and SCCWRP, 1980
4. Hershelman *et al.*,1980	11 Soule and Oguri, 1985	18 Ladd *et al.*, 1984
5 Hyperion Treatment Plant, original data	2 Soule and Oguri, 1986	19 Young *et al.*, 1975
6 CSDLAC, original data	13 Soule and Oguri, 1987	20 Liu and Schneider, 1988
7 CSDOC, original	14 Chen and Lu, 1974	21 Gersberg *et al.*, 1989
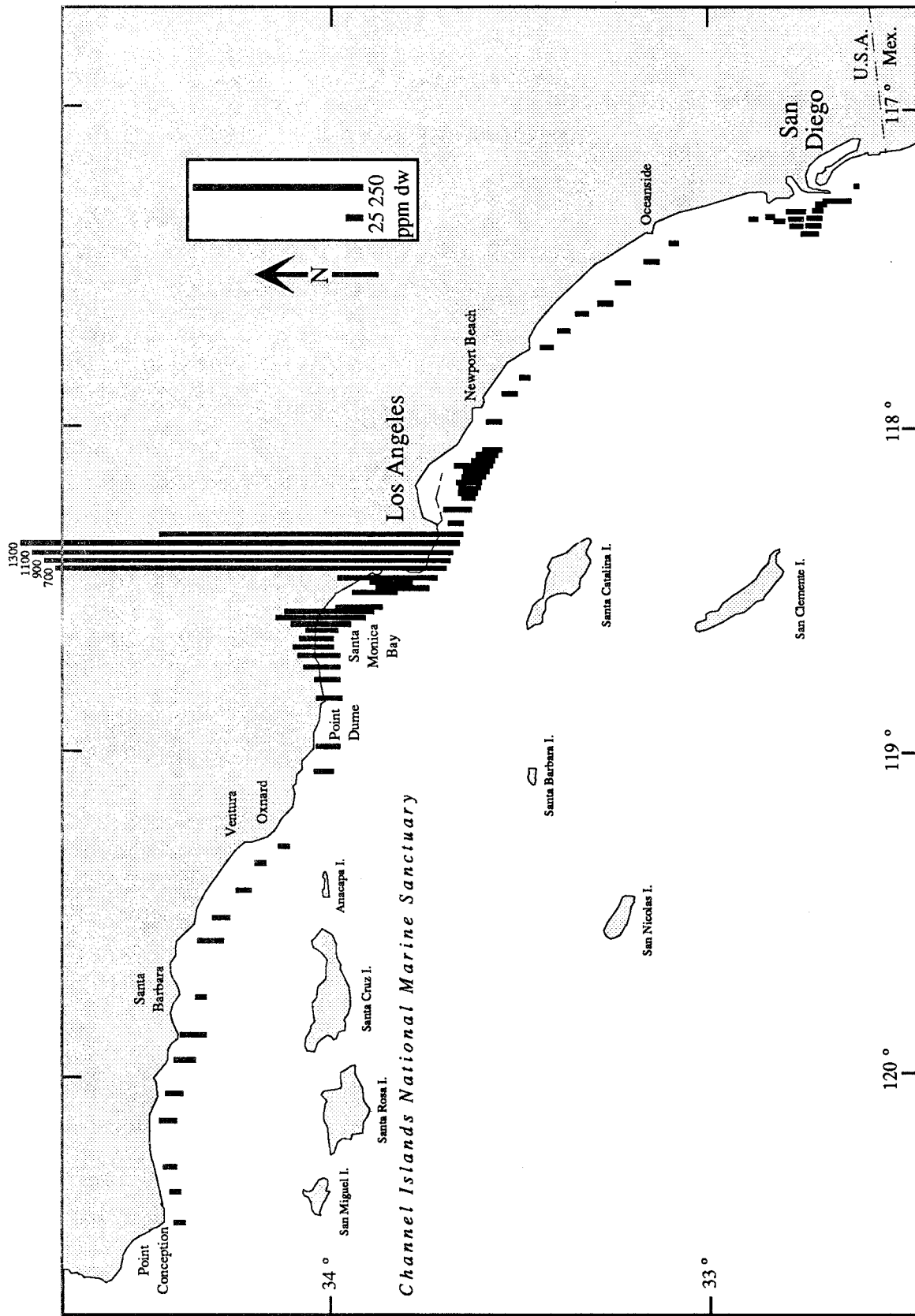
Figure 6.1. Chromium concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line, based on data from the 60-Meter Control Survey performed from April through August 1977 (Word and Mearns, 1979).
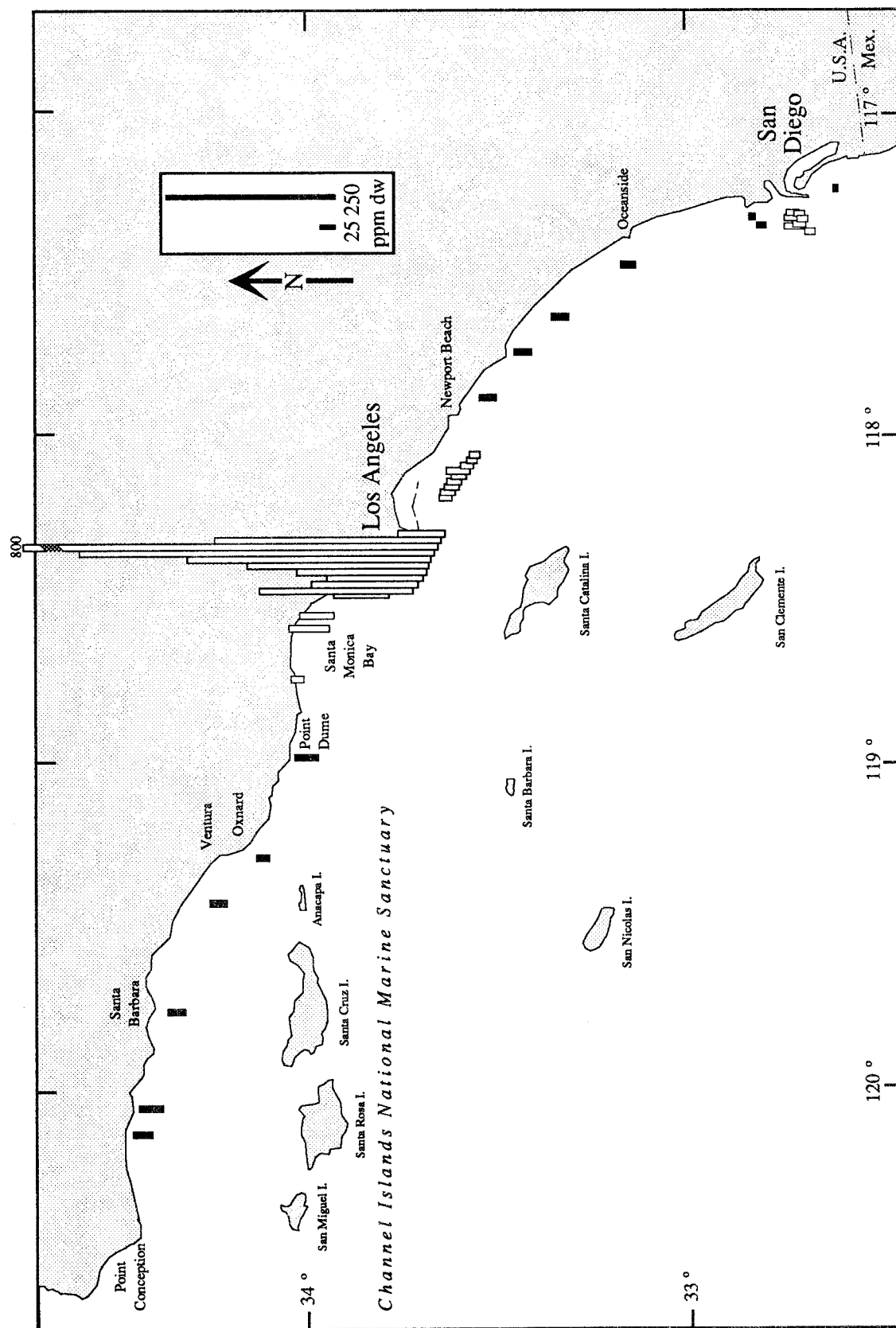
Figure 6.2. Chromium concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line for 1985; the black bars are based on data derived from Thompson, et al., 1987, while the white bars are based on data obtained from the various sanitation districts (City of Los Angeles, Los Angeles, Orange, and San Diego counties).
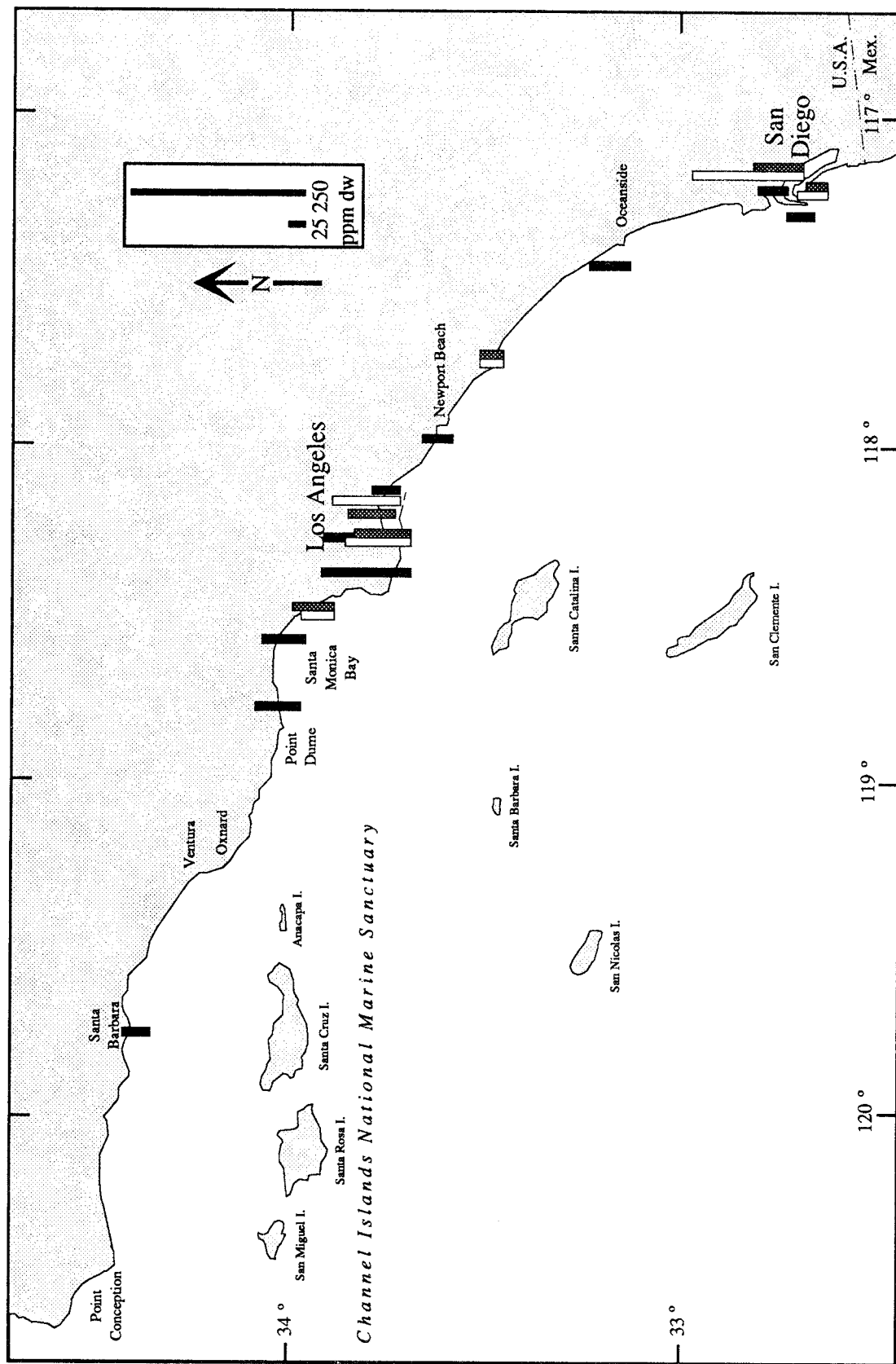
Figure 6.3. Chromium concentrations in the surficial sediments of the Southern California Bight based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 (☐) and 1985 (▨) and Mussel Watch Project for 1986 (▮) (NOAA, unpublished data and NOAA, 1988).

Table 6.2. Median sediment chromium concentrations and ratios to reference concentrations for 12 coastal areas, bays, or harbors in the Southern California Bight (from Table 6.1).

AREA	YEAR	MEDIAN	RANK (1)	RATIO TO REFERENCE (1)	RATIO TO REFERENCE (2)	RANK (2)
Palos Verdes Shelf	1985	273	1	9.4	9.4	3
San Diego Harbor	1983	113	2	3.9	18.8	1
Los Angeles-Long Beach Harbors	1978	87	3	3.0	14.5	2
Santa Monica Bay	1985	55	4	1.9	2.5	7
Marina del Rey	1987	41	5	1.4	6.8	4
Santa Barbara Shelf	1985	31	6	1.1	1.1	9
Port Hueneme to Point Dume	1985	31	7	1.1	1.1	9
Newport to Dana Point	1985	29	8	1.0	1.0	10
Newport shipyards	1986	31	7	1.1	5.2	5
San Pedro/Orange County Shelf	1985	24	9	0.8	0.8	11
Upper Newport Bay	1980	29	8	1.0	4.8	6
Dana Point to La Jolla	1985	22	10	0.8	0.8	11
Point Loma Shelf	1985	20	11	0.7	0.7	12
Tijuana Estuary, south arm	1988	9	12	0.3	1.5	8
Tijuana Estuary, north arm	1988	6	13	0.2	1.1	9

(1) Using a coastal reference of 29 ppm dw

(2) Bay and harbor ratios re-computed using a "bay" reference of 6 ppm dw.

Table 6.3 Summary of chromium concentrations (ppm dw) in whole *M. californianus* from various sampling areas in the Southern California Bight, 1980 and 1986, Phillips, 1988; NOAA, 1989.

Region of Site	Year	N	Mean	Median	Minimum	Maximum	SD	Source
Santa Monica Bay	1980	10	3.2	2.9	2.3	6.4	1.2	CMW
Santa Catalina Island	1980	5	4.2	3.4	1.2	10.2	3.6	CMW
Newport to Imperial Beach	1980	13	1.4	2.2	1.0	2.8	0.6	CMW
Point Dume	1986	3	2.5	2.6	2.2	2.8	–	NS&T
Santa Barbara Channel	1986	3	1.8	1.9	1.2	2.2	–	NS&T
All coastal sites	1986	8	1.5	1.3	1.0	2.2	–	NS&T

There is a considerable amount of information on the concentration of forms of dissolved chromium that are and are not toxic to marine organisms, but very little data on toxic levels in sediments. Circumstantial information based on field surveys of sediment concentrations, toxicity, and benthic community structure provide some indication of possibly toxic levels. For example, in studies along the Palos Verdes shelf, an ambient sediment chromium concentration as high as 478 ppm dw was not associated with mortality of amphipods, the benthic community remained undegraded at 305 ppm dw, and abundance of the pollution sensitive brittlestar, *Amphiodia urtica*, was unaffected at 94 ppm dw (Swartz *et al.*, 1986). In a national review of sediment concentrations of chromium associated with adverse biological effects, Long and Morgan (1990) calculated a probable effects range (ER-L to ER-M) of 80 to 145 ppm dw. The lower of these concentrations has been exceeded by median values at Santa

Monica Bay, Palos Verdes, Marina del Rey, San Diego Harbor, and Los Angeles-Long Beach harbors. The ER-M value was exceeded only at Palos Verdes.

Although chromium concentrations were high at Palos Verdes in 1985, they have, nonetheless decreased 71 percent over a 12-year period, from a 60-m isobath median of 1,030 ppm dw in 1974 to 296 ppm dw in 1985 (Figure 6.4). The decrease has been attributed largely to industrial source control actions (Stull and Baird, 1985). Over a similar period, sediment chromium concentrations around the Orange County outfall also decreased, from about 35 ppm dw in 1978-79 to 25 ppm dw in 1984-85 (CSDOC, 1986). Chromium concentration also appeared to decline by more than 55 percent in Marina del Rey over the 11-year period, 1977 through 1987 (Table 6.1), but the cause is unknown.

Chromium has been a regionwide anthropogenic contaminant of the northern and nearshore basins of the Bight since the early 1940s. In cores taken by Bruland et al. (1974), chromium concentrations and inferred inputs were relatively constant from the late 1700s through the 1930s, then began increasing during the 1940s. Schmidt and Reimers (1987) agree with this sequence of increasing contamination between 1940 and 1970; but, also found concentrations and inferred regionwide inputs leveling off during the 1970s and then decreasing during the mid 1980s. In cores from the Santa Monica Basin, Finney and Huh (1989) conclude that excess chromium inputs were detectable during the 1930s, peaked at levels twice background between 1960 and 1970, and have since decreased to mid-1980 concentrations about 1.2 to 1.3 times background. Both the post-1970 observations are consistent with the decrease reported on the Palos Verdes shelf (Stull and Baird, 1985). Changes in levels of chromium in sediment cores taken at Palos Verdes are consistent with decreases in sewage effluent (Stull et al., 1988).

CHROMIUM IN MUSSELS

Concentrations of chromium in digestive gland tissue of coastal mussels were measured at 16 sites by SCCWRP in 1971. Concentrations ranged from 0.8 ppm dw at San Nicolas Island to 61 ppm dw at Gaviota (Figure 6.5). The ratio of chromium in mussels from five coastal sites to three island sites was 9.0, suggesting a general trend of higher tissue concentrations for mainland sites. Elevated levels of chromium observed in mussels collected from Royal Palms (14 ppm dw) may have been a reflection of chromium inputs from the nearby JWPCP outfall, but sources for the other high values at Point Dume (14 ppm) and Gaviota (61 ppm dw) are difficult to explain. Alexander et al. (1976) postulated that oil tanker ballast water discharge could have accounted for the high concentrations at Gaviota.

The CMW Program has measured chromium in whole mussel tissue, less gonads, since 1977. Figure 6.6 illustrates the distribution of 163 results, from 1977 through 1985, by species and over ranges of concentrations. For both M. edulis and M. californianus, the greatest number of measurements fell in the range of chromium concentrations between 1.0 and 2.0 ppm dw . The next most frequently measured range for M. californianus was 2.0 to 3.0 ppm, while for M. edulis, it was 0-1.0 ppm.

Examination of these results by site location suggests some interesting patterns. Of the 28 measurements for chromium in M. californianus that exceeded 3.0 ppm, 16 (57%) occurred in mussels collected at Palos Verdes Peninsula sites, while 5 (18%) originated from Santa Catalina Island sites. As noted previously, municipal discharges have been identified as important sources of chromium to the aquatic environment, and bivalve mollusks have been shown to accumulate chromium to a moderate extent upon environmental exposure. Therefore, elevated concentrations in mussels from an area known to be impacted by a major municipal discharge is not surprising. However, the high concentrations at Santa Catalina Island sites are more surprising.

In the 1977 CMW surveys (spring and fall combined) average chromium concentrations in *M. californianus* were 3.4 (range 1.7 to 7.3) ppm dw at five coastal sites and 1.9 (range, 1.6 to 2.5) ppm dw at four island sites, yielding a coastal/island ratio of 1.8 which is only one-quarter of the ratio observed in 1971 at comparable sites. Thus, between 1971 and 1977, chromium concentrations in coastal mussels declined relative to concentrations in island mussels.
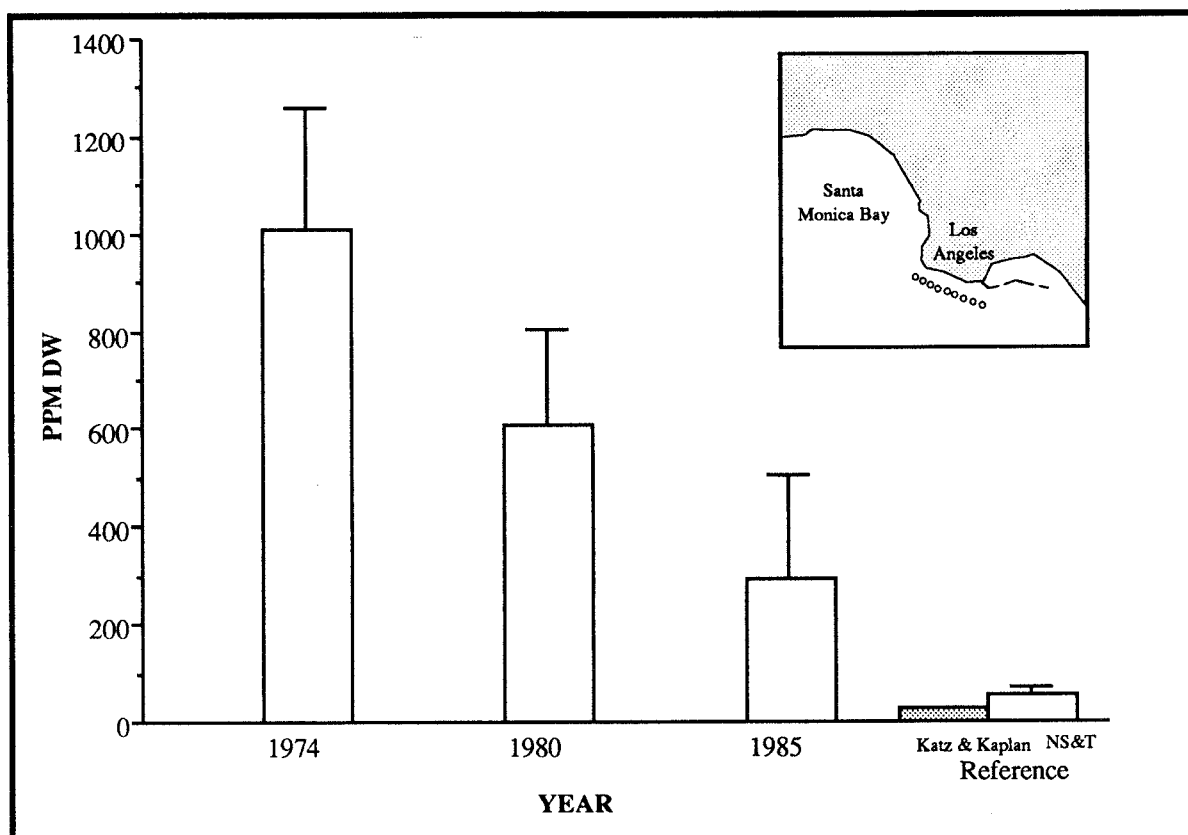
Figure 6.4. Mean chromium concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC. The reference values are based on the value reported by Katz and Kaplan (1981) and the mean of four relatively isolated NOAA NS&T sites in the Southern California Bight sampled between 1984 and 1986 (NOAA, 1988 and NOAA unpublished data). Inset shows approximate locations of sites sampled by CSDLAC.
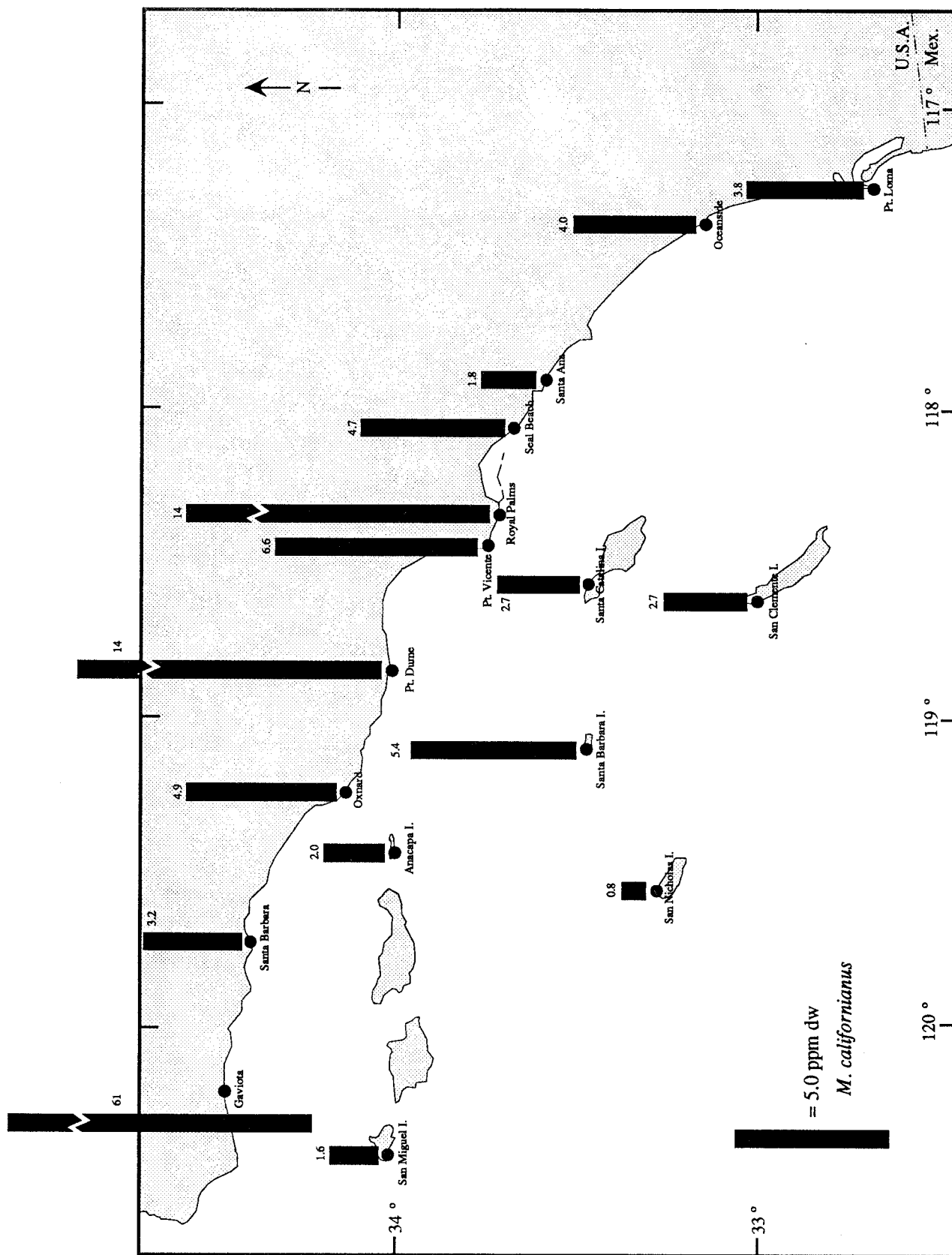
Figure 6.5. Chromium in digestive gland of mussels sampled in 1971. Values shown are means of six samples, each sample equals one individual.
Source: Alexander et al. (1976).
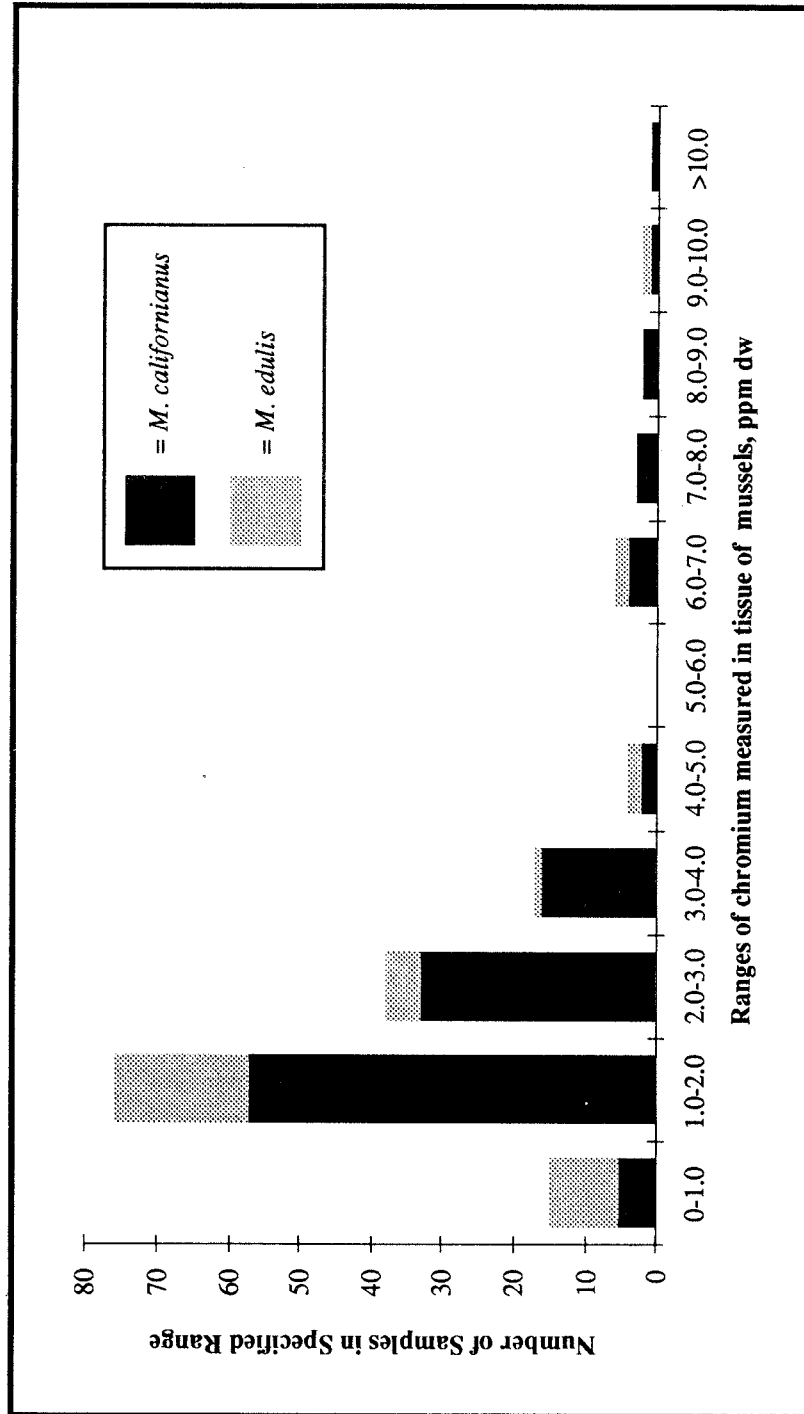
Figure 6.6. Distribution of sample measurements for chromium by species of resident southern California mussels. Source: Phillips, 1988.

In the 1986 NS&T Mussel Watch Project, chromium concentrations in whole *M. californianus* ranged from 0.99 ppm dw at Imperial Beach near San Diego, to 2.60 ppm at Royal Palms on the Palos Verdes shelf (Figure 6.7). The coastal/island gradient for *M. californianus* was much less dramatic in 1986 (1.2) compared to 1971 (9.0) and 1977 (1.8). In 1986, measurements of chromium in mussels from Royal Palms included the third highest chromium concentrations for *M. californianus* along the West Coast, and the seventh highest of any mussel or oyster site sampled nationally. However, it should be noted that the three highest chromium tissue burdens measured in the NS&T Mussel Watch Project were found in *M. edulis* from Marina del Rey. The source or sources of chromium to mussels in this location have not been identified, but possibilities include pigments or primer paints used on vessels, wood preservatives in marina building materials, or chromium residues in stormwater runoff draining into Marina del Rey.

Compared to other coastal areas, *M. californianus* from Santa Monica Bay had slightly elevated chromium concentrations. During 1980, the CMW sampled resident *M. californianus* at 28 southern California sites including 10 around the periphery of Santa Monica Bay. Chromium concentrations were higher at Santa Catalina Island (mean 4.2 ppm dw) and Santa Monica Bay (mean 3.2 ppm dw) than from 13 sites between the Newport jetties and Imperial Beach (mean, 1.4 ppm dw; Table 6.3). In the 1986 NOAA NS&T Mussel Watch Survey, chromium was also higher for samples from Point Dume (mean 2.5 ppm dw) than at three Santa Barbara Channel sites (mean 1.8 ppm dw) or all other southern California coastal sites (mean 1.5 ppm dw; Table 6.3).

The highest concentrations of chromium in whole resident *M. edulis* were found in Los Angeles-Long Beach harbors and in Marina del Rey during various sampling periods in the 1980s. While most harbor and bay regions or sites produced *M. edulis* with concentrations in the range of 1.0 to 1.7 ppm dw, 17 sites sampled in Los Angeles-Long Beach harbors between 1980 and 1985 produced an average chromium concentration of 3.5 ppm dw (range, 0.9 to 9.7 ppm dw; Table 6.4). With one exception, higher concentrations occurred at inner harbor sites than in the outer harbor (Figure 6.8). The highest concentration (9.7 ppm dw) occurred at a site near Terminal Island and the second highest (7.8 ppm dw) at the consolidated slip in the Dominquez Channel of inner Los Angeles Harbor. Earlier, results of the SCCWRP 1974 Harbors surveys indicated that the concentrations at the Los Angeles-Long Beach harbor sites (6.5 ppm dw), while elevated compared to reference sites (3 to 4 ppm dw), were still less than those at Royal Palms.
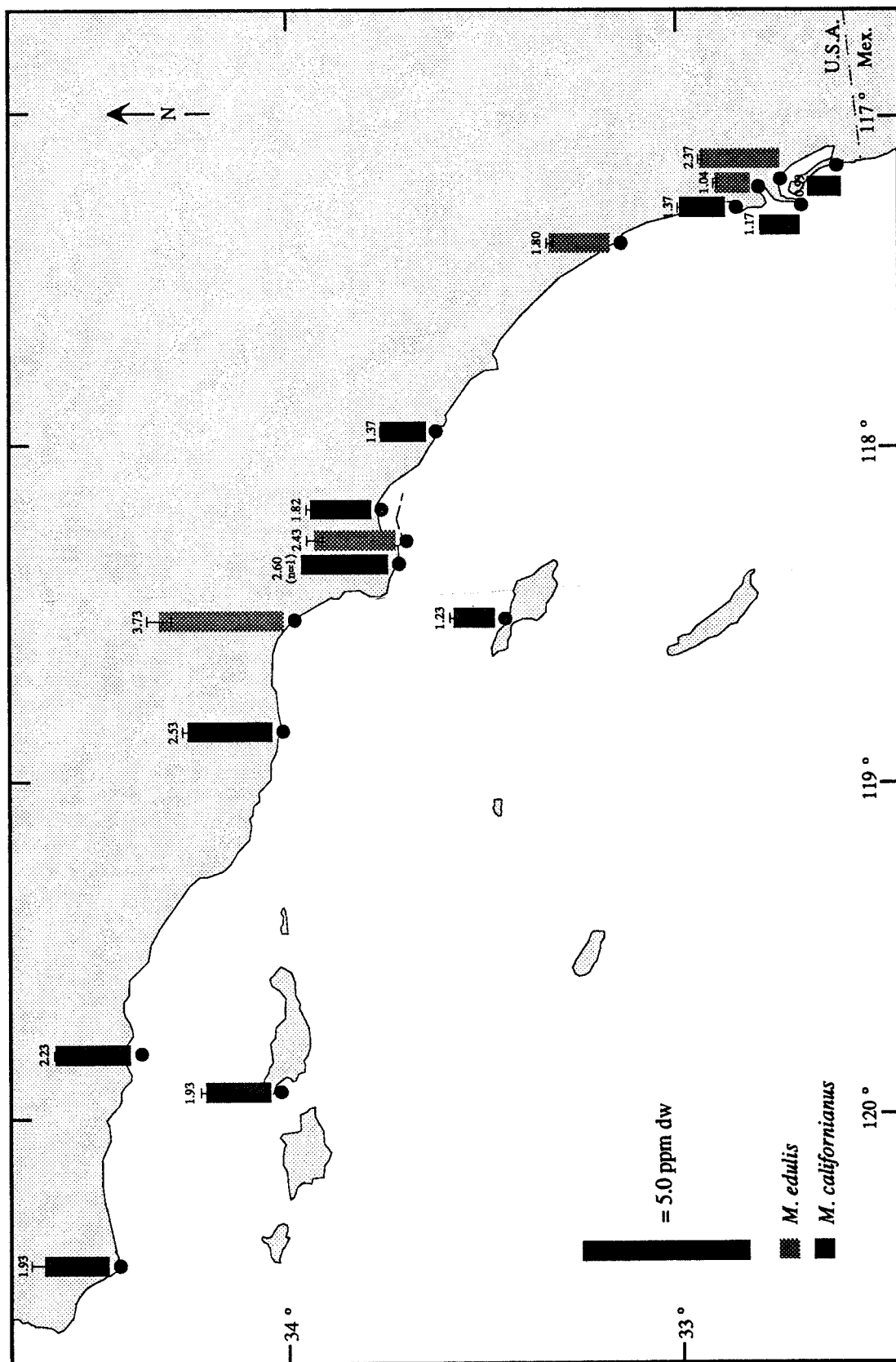
Figure 6.7. Chromium in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

Table 6.4 Summary of chromium concentrations (ppm dw) in whole *M. edulis* from various sampling areas in the Southern California Bight, 1980 through 1986, Phillips, 1988; NOAA, 1989.

Region or Site	Year	N[1]	Mean	Median	Min	Max	SD	Source
Channel Islands Harbor (Oxnard)	1980	1	0.4	–	–	–	–	CMW
Marina del Rey	1980, 1982	2	2.7	2.7	1.0	4.4	–	CMW
Marina del Rey	1986	3r	3.7	4.1	2.9	4.1	–	NS&T
Los Angeles-Long Beach harbors	1980, 1985	17	3.5	2.4	0.9	9.7	2.7	CMW
San Pedro breakwater	1986	3r	2.4	2.4	2.0	2.4	–	NS&T
Colorado Lagoon (Long Beach)	1982, 1985	3	1.2	0.8	0.8	1.8	–	CMW
Anaheim Bay	1980, 19882	2	1.7	1.7	1.0	2.4	–	CMW
Newport Bay	1980, 1985	5	1.1	1.1	0.9	1.4	–	CMW
Newport Pier	1980	1	1.2	–	–	–	–	CMW
Oceanside Harbor	1985	1	1.4	–	–	–	–	CMW
Mission Bay	1980, 1982	5	1.0	1.1	0.4	1.3	0.3	CMW
Point Loma	1983	1	1.7	–	–	–	–	CMW
San Diego Harbor	1980, 1982	4	1.4	1.6	0.6	1.8	0.5	CMW
San Diego Harbor jetty	1986	3r	2.3	2.3	2.3	2.5	–	NS&T

[1] r = replicates

Mean concentrations for several Marina del Rey sites were 2.7 ppm dw in 1980-82 and 3.7 ppm dw in the 1986 NOAA NS&T Mussel Watch survey (Table 6.4).

Resident *M. edulis* from several San Diego Harbor collections in 1980-82 contained low chromium concentrations (mean 1.4 ppm dw) relative to Los Angeles-Long Beach harbors (3.5 ppm) or Marina del Rey (3.7 ppm; Table 6.4). Likewise, *M. edulis* from sites in Newport Bay, Mission Bay, and the Channel Island Harbor (Oxnard) were relatively uncontaminated with chromium (0.4 to 1.1 ppm dw).

Ranking results from other studies in southern California also appear to emphasize the influence of municipal wastes as a source of chromium contamination in mussels. In the 1971 SCCWRP study, the Royal Palms site ranked second of 17 sites where digestive glands of *M. californianus* were analyzed. In a 1974 SCCWRP harbors study, six of the eight highest values (combining *M. edulis* and *M. californianus* results) occurred in coastal mussels at Royal Palms.

Overall mean and median levels of chromium in mussels sampled at all sites by NOAA's NS&T Program between 1986 and 1989 were similar for *M. edulis* (mean 1.961, median 1.684 ppm dw) and *M. californianus* (mean 1.912, median 1.600 ppm dw). Mean values at individual sites ranged from 0.397 to 13.936 ppm dw (*M. edulis*) and from 0.773 ppm dw to 9.2 ppm dw (*M. californianus*).
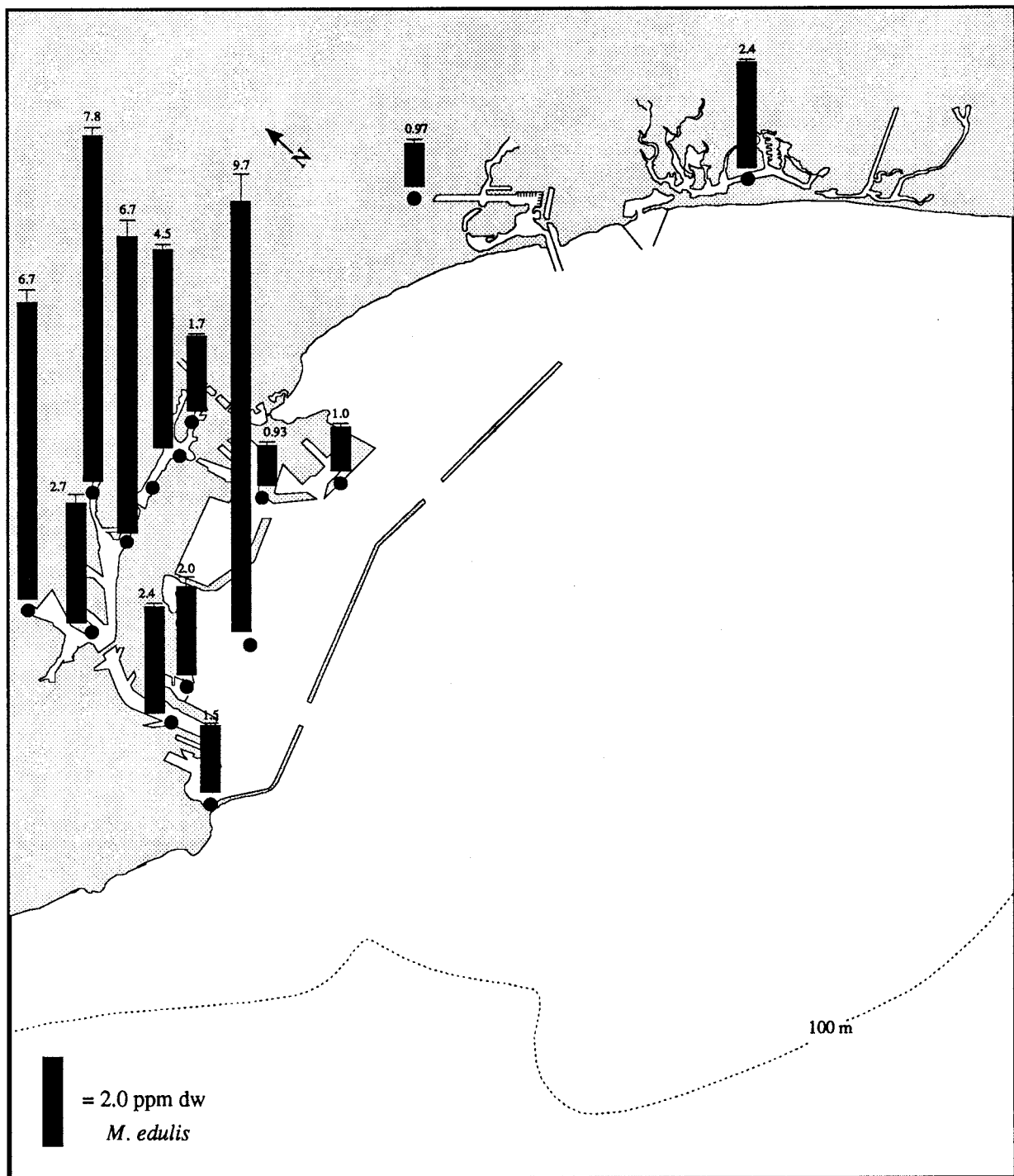
Figure 6.8. Chromium in whole soft body tissue, less gonads of mussels sampled in San Pedro Bay in 1982. Source: Phillips, 1988.

Long-term trends of chromium in *M. californianus* can be deduced from two southern California CMW sites sampled at least annually since 1977 (Table 6.5). At Royal Palms, concentrations fell from about 6 to 8 ppm dw in the late 1970s to about 3 to 4 ppm dw in the mid 1980s (p = 0.0014, r^2 = 0.697, Figure 6.9). This decline was correlated with a decrease in chromium mass emission rates from the nearby CSDLAC Whites Point sewage outfall (p - 0.05, r_s = 0.743, using only late-year mussel values when more than two sampling periods occurred in one year). This supports the hypothesis that at least part of the chromium in Royal Palms mussels came from sewage effluent and that source control effectively reduced concentrations in these mussels. By contrast, there was no statistically significant trend over a decade of monitoring *M. californianus* at Oceanside (r^2 = 0.16, p = 0.175). However, inspection of CMW data reveals that if one value of 2.6 ppm dw in November 1978 is excluded, concentrations increased from about 1.0 to 1.2 ppm dw in 1977 to about 1.8 ppm dw in 1986 (r^2 = .826, p = 0.0001). Thus, while chromium concentrations have always been very low at Oceanside, there is some indication that they may be increasing. Examination of data from a third long-term CMW monitoring site at Montana de Oro State Park in San Luis Obispo County, 100 km north of Point Conception, resulted in chromium concentrations ranging from 1.1 to 3.5 ppm dw with no significant long-term trend between 1977 and 1987 (r^2 =- 0.22, p = 0.52, data not shown). NOAA's NS&T Mussel Watch Project documented decreases in chromium concentrations in mussels from Oceanside, Marina del Rey, and Point Dume between 1986 and 1988 (NOAA, 1989).

Table 6.5. Comparison of chromium mass emissions from JWPCP and chromium measured in mussel tissue at CMW Royal Palms site, by year. Sources: Phillips, 1988 and SCCWRP, 1986.

Year	Chromium Mass Emission, JWPCP (mt/yr)	Chromium in *M. californianus*, Royal Palms site (ppm dw)
1977	176	6.7
1978	162	6.4
1979	130	8.5
1981	106	3.4
1982	94	3.7
1983	70	3.4
1984	53	3.9
1985	40	3.3

In summary, it appears that chromium has been elevated in mussels from some urban areas and that concentrations in mussels at Royal Palms have declined from nearly 10 times background in 1971 to near (2 times) background in the mid 1980s. Long-term monitoring is needed to confirm trends in all other urban areas and to confirm the possibility of increases at Oceanside.
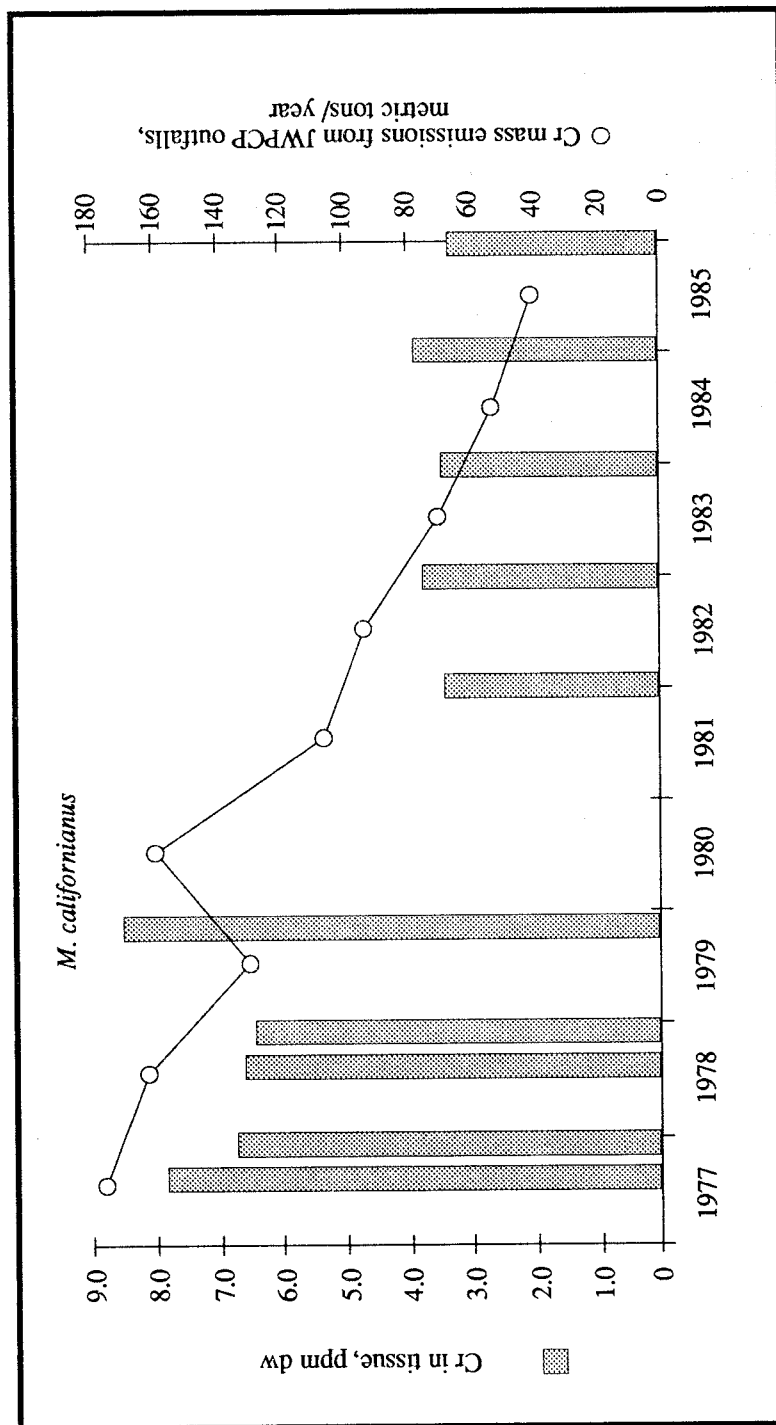
Figure 6.9. Comparison of JWPCP annual mass emissions of chromium vs. concentrations of chromium in tissue of mussels sampled at Royal Palms, 1977-1985. Sources: SCCWRP, 1986 and Phillips, 1988.

CHROMIUM IN FISH AND OTHER SPECIES

Chromium has been measured in flesh or other edible tissues of at least 32 species of fish and macroinvertebrates including 4 species of mollusks, 5 crustaceans, 18 finfish, and 4 sharks, as well as in kelp. In the survey data selected for this report, concentrations ranged from 0.003 ppm ww in Pacific bonito collected off Orange County in 1980-81 to 2.24 ppm ww in a collection of black abalone collected from Palos Verdes during a 1975-77 seafood study (6). In general, concentrations were higher in macroinvertebrates (0.01 to 2.24 ppm ww) and sharks (0.004 to 0.298 ppm ww) than in all fish (0.003 to 0.123 ppm ww) except in juvenile mullet (0.008 to 0.559 ppm ww). The lowest average concentration was 0.006 ppm ww in muscle of white croaker collected from the Palos Verdes shelf in 1980 and the highest was 1.354 ppm ww in black abalone collected from Palos Verdes during the 1975-77 SCCWRP seafood survey (Table 6.6).

Muscle tissue of at least 10 species of fish did not show higher concentrations of chromium in areas with chromium-contaminated sediments or receiving known inputs of chromium. However, chromium concentrations were elevated in four of five species of macroinvertebrates from Palos Verdes or near Orange County's outfall relative to other coastal/island control or reference sites during the 1975-77 SCCWRP seafood survey. The greatest elevations in contamination compared to reference sites (more than 5-fold) were reported in mollusks (black abalone and purple-hinge scallop), moderate elevations (2- to 4-fold) occurred in two of three crustaceans (ridgeback prawn and yellow crab), concentrations were lower by half in California spiny lobster from Palos Verdes than in similar samples from San Diego, and there were no elevations in five species of fish (Table 6.7).

Results reported by de Goeij et al. (1974) indicate that chromium concentrations in composites of liver tissue from Dover sole collected from 17 coastal and island sites in 1971-72 ranged from 0.07 to 0.08 ppm ww in fish from three sites (Palos Verdes; Orange County; and West End, Santa Catalina Island) to 0.245 in fish collected off the Port Hueneme area (Figure 6.10). The second highest concentration was 0.2 ppm ww in fish from the outer or southwestern side of Santa Catalina Island. Concentrations in four of five sites along the chromium-contaminated Palos Verdes shelf yielded average concentrations less than 0.01 ppm ww. As a consequence, there was no positive relationship between chromium content of sediments and chromium in livers of fish. There may have been an inverse or negative relationship (de Goeij et al., 1974).

A similar pattern emerged from 1984 NOAA NS&T Benthic Surveillance data. For hornyhead turbot, mean concentrations ranged from 0.103 ppm ww in fish from Santa Monica Bay to 0.234 in fish from the Dana Point reference site, with intermediate values at San Pedro Canyon near Palos Verdes (0.117 ppm ww) and in San Diego Bay (0.148 ppm ww). Likewise, chromium in liver from barred sand bass and white croaker from Dana Point were slightly higher than in comparable specimens from more contaminated sites in San Diego Harbor and Seal Beach, respectively (Figure 6.11).

There is no U. S. seafood action limit or criteria for chromium. The only seafood quality criteria reported in Nauen (1983) is 1.0 ppm ww for Hong Kong. With the exception of black abalone collected from Palos Verdes during 1975-77, no seafood organisms from the Bight contained wet weight chromium concentrations in excess of this value.

Table 6.6. Chromium concentrations (ppm ww) in edible tissues of selected organisms from the Southern California Bight.

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	Data Source
Kelp	Los Angeles Harbor	1980	5	0.124	0.126	0.091	0.145	0.020	Young and Mearns, 1980
Mysids (whole)	Palos Verdes	1980	8	0.994	0.874	0.271	2.110	0.583	Schafer et al., 1980
Zooplankton (whole)	Coastal	1980-81	5	0.110	0.078	0.020	0.225	0.081	Schafer et al., 1980
Black Abalone	Palos Verdes	1975-77	3	1.354	0.950	0.872	2.240	0.768	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.075	0.095	0.036	0.095	0.034	Young et al., 1978
Gaper Clams	Los Angeles Harbor	1980	5	0.076	0.071	0.063	0.100	0.015	Young and Mearns, 1980
Market Squid	Coastal	1980-81	3	0.040	0.036	0.033	0.042	0.005	Schafer et al., 1980
Purple-hinge Scallop	Palos Verdes	1975-77	8	0.305	0.260	0.133	0.590	0.169	Young et al., 1978
	Santa Barbara	1975-77	2	0.012	0.012	0.010	0.014	0.003	Young et al., 1978
	Santa Catalina Island	1975-77	4	0.076	0.048	0.039	0.170	0.063	Young et al., 1978
California Spiny Lobster	Palos Verdes	1975-77	3	0.021	0.024	<0.017	0.029	0.011	Young et al., 1978
	San Diego	1975-77	3	0.042	0.029	0.011	0.086	0.039	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.016	<0.018	0.011	0.029	0.011	Young et al., 1978
Ridgeback Prawn	Palos Verdes	1975-77	3	0.015	<0.019	<0.016	0.026	0.010	Young et al., 1978
	Orange County	1975-77	3	0.091	0.123	0.016	0.133	0.065	Young et al., 1978
	Dana Point	1975-77	3	0.021	0.020	0.018	0.024	0.003	Young et al., 1978
	Palos Verdes	1980	5	0.188	0.155	0.115	0.364	0.101	
Yellow Crab	Palos Verdes	1975-77	3	0.075	0.080	0.051	0.094	0.022	Young et al., 1978
	Dana Point	1975-77	3	0.038	0.040	<0.018	0.064	0.028	Young et al., 1978
Boccacio	Palos Verdes	1975-77	3	0.018	0.010	0.009	0.034	0.014	Young et al., 1978
	Orange County	1975-77	3	0.021	0.020	0.016	0.028	0.006	Young et al., 1978
	San Clemente Island	1975-77	3	0.016	<0.014	0.014	0.026	0.009	Young et al., 1978
California Halibut	Palos Verdes	1975-77	2	0.015	0.015	0.015	0.015		Young et al., 1978
	Point Dume	1975-77	2	0.017	0.017	<0.014	0.027	0.014	Young et al., 1978
	Los Angeles Harbor	1980	4	0.032	0.026	0.022	0.055	0.015	Young and Mearns, 1980
California Scorpionfish	Palos Verdes	1975-77	3	0.035	0.036	0.032	0.036	0.002	Young et al., 1978
	Orange County	1975-77	3	0.075	0.068	0.066	0.092	0.014	Young et al., 1978
	Dana Point	1975-77	3	0.055	0.037	0.016	0.113	0.051	Young et al., 1978
	Palos Verdes	1980	4	0.015	0.016	0.010	0.018	0.004	Schafer et al., 1980
Dover Sole	Palos Verdes	1980	5	0.015	0.005	0.005	0.051	0.020	Schafer et al., 1980
Northern Anchovy	Los Angeles Harbor	1980	5	0.032	0.032	0.030	0.036	0.003	Young and Mearns, 1980
	Coastal	1980-81	5	0.068	0.069	0.026	0.105	0.029	Schafer et al., 1980
Pacific Bonito	Orange County	1980-81	5	0.037	0.042	0.003	0.065	0.027	Schafer et al., 1980
Pacific Hake	Coastal	1980-81	5	0.072	0.066	0.004	0.130	0.050	Schafer et al., 1980
Pacific Mackerel	Coastal	1980-81	6	0.032	0.030	0.019	0.047	0.010	Schafer et al., 1980
Pacific Sanddab	Palos Verdes	1975-77	3	0.032	0.032	0.019	0.046	0.014	Young et al., 1978
	Orange County	1975-77	3	0.033	0.031	0.024	0.045	0.011	Young et al., 1978
	Dana Point	1975-77	3	0.022	0.024	0.015	0.028	0.007	Young et al., 1978
	Samta Catalina Island	1975-77	3	0.055	0.064	0.023	0.077	0.028	Young et al., 1978
Pacific Sardine	Coastal	1980-81	5	0.035	0.035	0.016	0.064	0.020	Schafer et al., 1980
Spotted Sand Bass	Newport Bay	1978	3	0.013	0.014	0.005	0.019	0.007	Young and Mearns, 1980b
Striped Bass	Newport Bay	1978	3	0.004	0.005	0.004	0.005	0.000	Young and Mearns, 1980b
Striped Mullet (adult)	Newport Bay	1978	3	0.020	0.016	0.013	0.030	0.009	Young and Mearns, 1980b
Striped Mullet (juvenile)	Newport Bay	1978	3	0.198	0.018	0.018	0.559	0.312	Young and Mearns, 1980b
Swordfish	Coastal	1980-81	5	0.017	0.023	0.004	0.027	0.010	Schafer et al 1980
Topsmelt	Newport Bay	1978	3	0.011	0.005	0.005	0.023	0.010	Young and Mearns, 1980b
White Croaker	Palos Verdes	1975-77	3	0.063	0.059	0.058	0.073	0.008	Young et al., 1978
	Orange County	1975-77	3	0.062	0.063	0.056	0.066	0.005	Young et al., 1978
	Dana Point	1975-77	3	0.065	0.040	0.031	0.123	0.051	Young et al., 1978
	Los Angeles Harbor	1980	5	0.019	0.017	0.006	0.035	0.011	Young and Mearns, 1980
	Palos Verdes	1980	4	0.006	0.006	0.006	0.007	0.001	Shafer et al., 1980
Yellowfin Croaker	Newport Bay	1978	3	0.009	0.008	0.004	0.014	0.005	
Spiny Dogfish	Palos Verdes	1980	5	0.030	0.035	0.004	0.042	0.015	Schafer et al., 1980
Mako Shark	Coastal	1980-81	5	0.073	0.058	0.013	0.131	0.047	Schafer et al., 1980
Thresher Shark	Coastal	1980-81	5	0.071	0.059	0.007	0.192	0.071	Schafer et al., 1980
White Shark	Coastal	1980-81	3	0.145	0.087	0.050	0.298	0.134	Schafer et al., 1980

Table 6.7. Summary of total chromium concentrations (ppm ww) in muscle or edible tissue of seafood organisms from several locations in the Southern California Bight, 1975-77.

COMMON NAME	COASTAL SITES					ISLAND SITES		
	POINT DUME	PALOS VERDES	SAN PEDRO BAY/OCSD	DANA POINT	SAN DIEGO	SANTA CATALINA	SAN CLEMENTE	SANTA BARBARA
Black abalone	--	1.354 ±0.768 (3)	--	--	--	0.075 ±0.034 (3)	--	--
Purple-hinge scallop	--	0.305 ±0.169 (3)	--	--	--	0.076 ±0.063 (4)	--	0.012 ±0.003 (2)
Yellow crab	--	0.075 ±0.022 (3)	--	0.038 ±0.028 (3)	--	--	--	--
California spiny lobster	--	0.021 ±0.011 (3)	--	--	0.042 ±0.039 (3)	0.016 ±0.011 (3)	--	--
Ridgeback prawn	--	--	0.091 ±0.065 (3)	0.021 ±0.003 (3)	--	--	--	--
Pacific sanddab	--	0.032 ±0.014 (3)	0.033 ±0.031 (3)	0.022 ±0.007 (3)	--	0.055 ±0.028 (3)	--	--
California halibut	0.017 ±0.014 (2)	0.015 ±0 (2)	--	--	--	--	--	--
White croaker	--	0.063 ±0.059 (3)	0.062 ±0.005 (3)	0.065 ±0.051 (3)	--	--	--	--
California scorpionfish	--	0.035 ±0.002 (3)	0.075 ±0.014 (3)	0.055 ±0.051 (3)	--	--	--	--
Bocaccio	--	0.018 +0.014 (3)	0.021 ±0.006 (3)	--	--	--	0.016 ±0.009 (3)	--
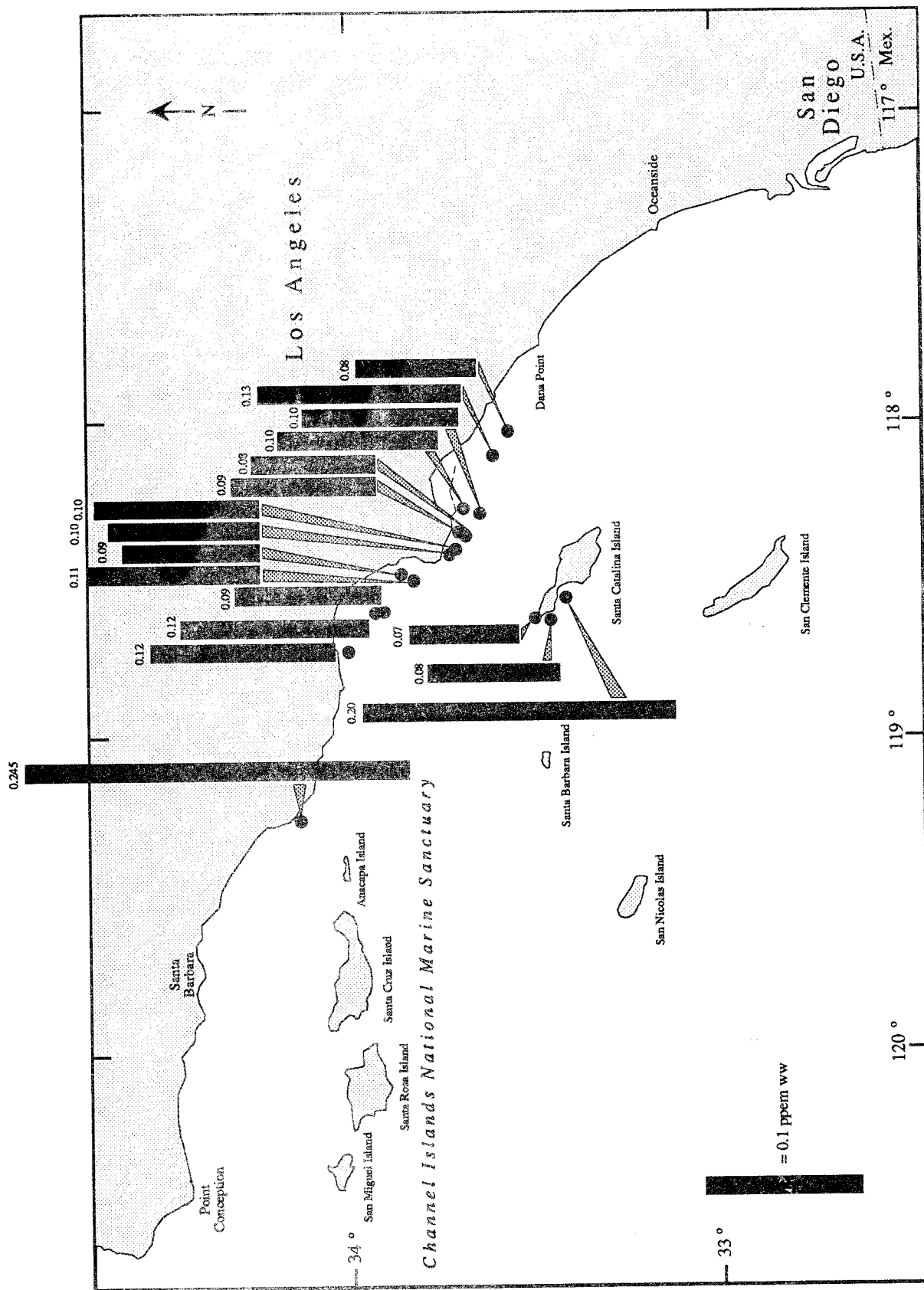
Figure 6.10. Chromium concentrations (ppm ww) in liver tissue of Dover sole collected in the Southern California Bight in 1971-72. Source: de Goeij et al. (unpublished).
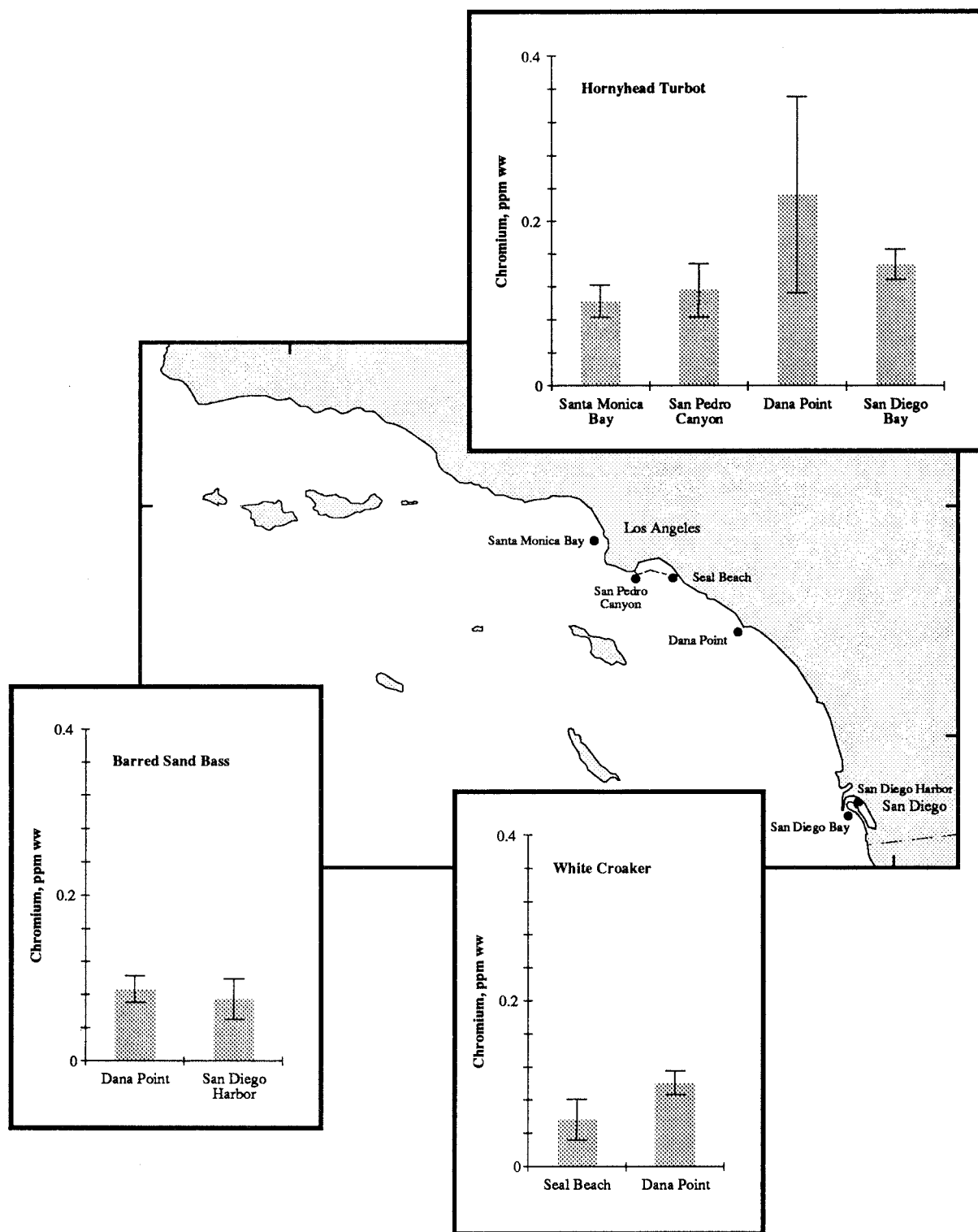
Figure 6.11. Concentrations of chromium measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

SUMMARY AND CONCLUSIONS

In the past, chromium in sediments of the Southern California Bight has been greatly elevated (more than 10-fold) at Palos Verdes, moderately elevated (greater than 3-fold) in San Diego and Los Angeles harbors, and slightly elevated (1.5- to 3-fold) in Santa Monica Bay and Marina del Rey. By comparison, sediments from all other coastal shelf and bay areas, including sewage discharge sites (Orange County, Point Loma) have had chromium concentrations at or near background levels. Sediment types and depth vary greatly among the regions compared here, and since chromium concentrations are highly dependent on these features, it is possible past gradients are controlled more by these features than by variations in chromium inputs.

In 1971, samples of mussel digestive gland demonstrated a strong, large-scale, order-of-magnitude gradient of increasing chromium concentrations with proximity to the mainland coast and the Los Angeles area. Based on values from whole mussels, the regional gradient was much weaker during the 1980s (only 2-fold). Stronger (10-fold) gradients occurred only within Los Angeles-Long Beach harbors. Elsewhere, including at Royal Palms near the Los Angeles County sewage discharge site, concentrations were too low and variable to identify regional point sources that would control levels of chromium in mussels. The best way to document a long-term regionwide decline is to re-sample digestive glands in mussels from sites previously surveyed by SCCWRP in 1971 and 1974. Nevertheless, data from Royal Palms indicates a long-term decline in mussel contamination has occurred at that site.

Chromium has not accumulated in tissues of fish and several invertebrates in response to inputs or well-documented sediment gradients. Further, chromium does not undergo biomagnification in marine food webs of the Bight and may actually decrease with trophic level.

In contrast to fish and lobster, abalone, scallop, yellow crab, and ridgeback prawn have, like mussels, experienced chromium contamination principally at Palos Verdes. These observations were made mainly between 1975 and 1977. No comparable collections have been made in the 1980s. Presumably concentrations have declined in these seafood organisms, but only renewed sampling can confirm this. If it can be shown that concentrations in abalone from Palos Verdes have declined since 1975-77, then it is possible that no seafood organisms from the Bight now exceed the only available international criteria of 1.0 ppm ww.

INFORMATION NEEDS

Abalone, scallops, yellow crab, ridgeback prawn, and mussels (including separate analyses of digestive glands) from Palos Verdes and appropriate reference sites should be re-sampled to determine whether source controls implemented by CSDLAC have resulted in decreases in chromium concentrations. Likewise, mussels from Los Angeles-Long Beach harbors should be re-surveyed to see if elevated levels in inner harbor areas persist or have declined. Finally, chromium in livers of previously sampled fish species from several Los Angeles area sites should be sampled to see if low levels still exist or if concentrations have increased to reference-area levels.

CHAPTER 7
COPPER

Because copper is an important industrial material, it has a great number of anthropogenic sources to the marine environment. These include municipal discharges, copper smelting and mining, and copper-based algicides, fungicides, and antifouling paints. Mining and burning of coal may also result in copper input to the environment. Municipal discharges can represent an amalgam of many sources collected by the treatment system, such as metal cleaning operations, plating baths and rinses, commercial pigments and dyes, wood preservatives, and leaching from copper piping (Netzer and Beszedits, 1979). One isolated source of importance in south San Diego Harbor is a bulk ore-loading operation for copper concentrate (chalcopyrite). An increase in sediment concentrations of copper in the area from 110 ppm, before the ore-loading activity began, to 13,000 ppm in 1984 has been documented by the California Regional Water Quality Control Board (San Diego Interagency Water Quality Control Board (SDIWQCB), 1989). Finally, copper was used extensively in vessel antifouling paints before the advent of tributyl tin in the mid-1970s. Tributyl tin paints are now restricted (see chapter 12) and new copper formulations are being recommended to replace them (Paul and Davies, 1986).

Copper is widely distributed in the natural environment. Although it is necessary in several enzyme reactions and is a biologically essential element, it also demonstrates acute toxicological effects occurring at small concentration increments above essential levels (Eisler, 1981; Scott and Major, 1972). In contrast to the low observed toxicity observed in mammalian species exposed to the element through ingested water, copper is exceedingly toxic to aquatic biota. For invertebrates and fish, the most significant uptake mechanism is through respiration. Hodson et al. (1979) portrayed the toxic effects of respiratory copper uptake through gills of aquatic organisms as analogous to mammalian sensitivity to airborne metals.

Mollusk species not only concentrate copper in their soft body tissue, but also accumulate it to higher levels than any other group of marine plant or animal organisms (Eisler, 1981). Scott and Major (1972) found that field-collected M. edulis accumulate copper to levels approximating those of laboratory specimens exposed to high concentrations. They also suggested that copper was bound in relatively innocuous organic forms in that species. This was confirmed by later work focusing on metallothionein, which is a low molecular weight protein capable of binding metals such as zinc, cadmium, copper, and mercury, and which are found in a diversity of species. Metallothionein has been studied extensively in mussels (Roesijadi et al., 1982).

There is a considerable amount of data concerning levels of dissolved copper species and compounds that are toxic to or lead to bioaccumulation in marine plants, invertebrates, and fish (Eisler, 1981; Hodson et al., 1979) and concerning specific sublethal effects on mussels (Akberali et al., 1985; Sunila, 1986; Sunila and Lindstroem, 1985; Grace and Gainey, 1987). However, there is very little data on biological consequences of exposures to copper through sediments or in tissues of food organisms. It is interesting that although increasing salinity would be expected to decrease copper toxicity (both acute and lethal) due to complexing of copper ions, the results of toxicity studies indicate marine fish species to be as sensitive as freshwater species.

Young et al. (1979) attempted to quantify anthropogenic copper inputs into the Southern California Bight. They estimated that in 1971, 510 mt per year (67%) originated from five major municipal outfalls, 180 mt per year (24%) from vessel antifouling paints, 40 mt per year (5.3%) from storm runoff, and 30 mt per year (3.9%) from aerial fallout. Thus, copper-based antifouling paints may have been a significant chronic source in the southern California region, particularly in those localities with commercial or recreational boating. As noted above, restrictions on tin antifouling paints may lead to a resurgence of copper-based coatings. Since 1971, sewage emissions of copper have decreased 50 percent to 240 mt per year in 1985 (SCCWRP, 1987a) and 135 mt in 1987 (SCCWRP, 1988). However, runoff of the Los Angeles River carried 9 mt of copper in 1971-72 and 15 mt in 1985-86 (Schafer and Gossett, 1988). By comparison, the Pacific Baroness sank off Point Conception in September 1987 with a cargo of 21,000 mt of copper concentrate (Hyland et al., 1989).

COPPER IN SEDIMENTS

Copper has been analyzed in thousands of coastal, bay, and harbor sediments from the Southern California Bight. Concentrations have ranged from 2.3 ppm dw at a site surveyed in 1977 along the Santa Barbara coast, to 20,300 ppm dw at a site sampled in 1972 near a boat yard in Newport Bay (Liu and Schneider, 1988). The latter is the highest concentration encountered in U.S. coastal marine sediments. Nearly comparable concentrations have been reported near ore spill sites in San Diego Harbor (WESTEC Services, 1986). Concentrations in outfall areas of the coastal shelf have ranged from 5.9 ppm dw near Point Loma, to 782 ppm dw at a site off Palos Verdes sampled in 1977 (Table 7.1).

Copper concentrations in shelf sediments are highly dependent on depth or depth-related factors. In samples collected off the relatively uncontaminated coast between Point Dume and Port Hueneme over a depth range of 14 to 745 m, copper concentrations varied directly and significantly ($p<0.001$) with depth volatile solids and percent silt and inversely and significantly with percent dry weight (Hershelman et al., 1982). Average copper concentrations increased from 4.1 ppm dw in the depth range of 14 to 30 m to 27 ppm dw in the depth range of 713 to 745 m (computed from data in Hershelman et al., 1982). The average concentration along the 60-m isobath (45 to 62 m) was 11.2 ppm dw; a value in good agreement with the regionwide 1977 60-m coastal control mean of 9.1 ppm dw.

The "background" or reference copper concentration on the coastal shelf appears to be about 10 ppm dw. This is the approximate mean and median value for all 1977-85 surveys in rural coastal shelf areas (Table 7.1) and about midway between the "control" value of 9 ppm dw computed for the 60-m transect by Word and Mearns (1979) and the value of 12.5 ppm dw computed for background shelf sites by Katz and Kaplan (1981) from total copper data in Chow and Earl (1979).

The overall mean concentration of copper in sediments at all sites sampled by NOAA's NS&T Program between 1984 and 1989 is higher than the background and control levels calculated from other surveys. The overall mean was 29.408 ppm dw, while the median value was 15.675 ppm dw. Site means ranged from 1.03 ppm dw to 246.33 ppm dw.

Along the coastal shelf, control or reference 60-m isobath surveys in 1977 and 1985 indicated that very similar patterns of contamination prevailed over the 8-year interval (Figures 7.1 and 7.2) with slightly elevated concentrations in Los Angeles-Long Beach harbors and greatly elevated concentrations off the Palos Verdes sewage discharge area. A second epicenter of elevated copper occurred at one station each in 1977 and 1985 at or south of Point Loma near San Diego.

No data have been encountered suggesting background or reference levels in sediments of bays, harbors, or lagoons. In data collected through 1986, the lowest mean was 16 ppm dw in Upper Newport Bay sampled in 1970 (Table 7.1). The median there was 22 ppm dw. However, in a 1988 survey of sediments of the Tijuana Estuary, Gersberg et al. (1989) reported copper concentrations ranging from 0.6 to 35.0 ppm dw, median concentrations were 12.7 ppm dw in the south arm (range 0.7 to 25.3), 2.3 ppm dw in the north arm (range 1.0 to 35), and only 0.9 ppm dw in the mouth (range 0.6 to 1.4). With such differences existing between and within non-industrialized bays and lagoons, it is difficult to suggest reference values for contrasting with more industrialized harbor areas. Mean copper concentrations at sites in two other recreational harbors in 1983 and 1984 were 44.7 ppm dw (range 36 to 51) at the west entrance of Huntington Harbor and 48.3 ppm dw (range 26 to 80) at the launch ramp in Dana Harbor (OCEMA, 1986). By contrast, mean concentrations for other harbors ranged from 88 ppm dw in Marina del Rey in 1978 (Soule and Oguri, 1980b) to 9,488 ppm dw in Lower Newport Bay sampled in 1972 (Young et al., 1975).

Figure 7.1. Copper concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line, based on data from the 60-Meter Control Survey performed from April through August 1977 (Word and Mearns, 1979).
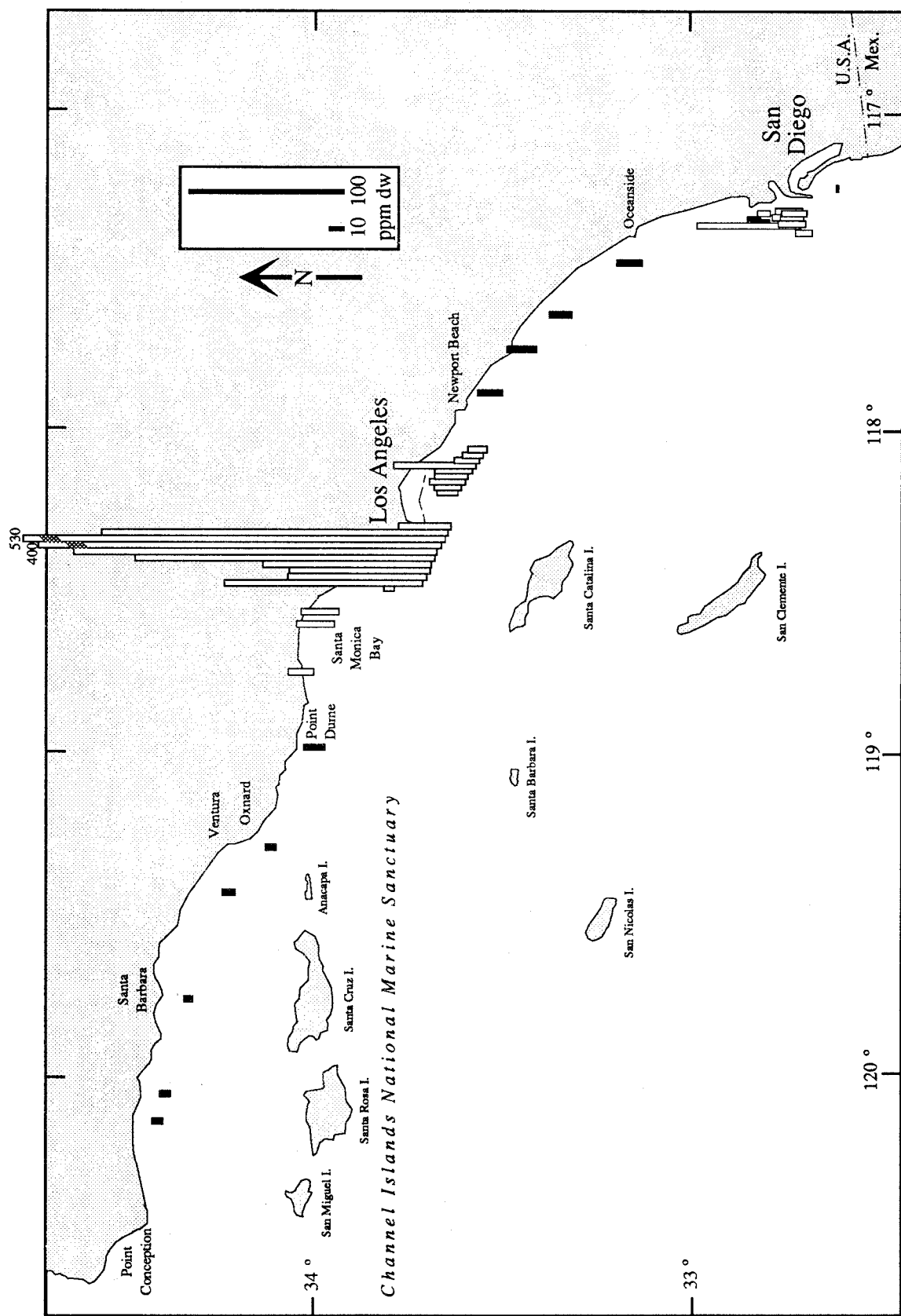
Figure 7.2. Copper concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line for 1985; the black bars are based on data derived from Thompson et al., 1987, while the white bars are based on data obtained from the various sanitation districts (City of Los Angeles, Los Angeles, Orange, and San Diego counties).

Table 7.1. Mean, median, minimum, and maximum copper concentrations in surface sediment from selected surveys, 1970-85 in ppm dw.

SITE	Year	N	Mean	Median	Min	Max	SD	SOURCE
Rural Coastal Shelf (60 meters only):								
Santa Barbara shelf	1977	11	9.2	5.4	2.3	40	11	1
	1985	4	6.5	6.5	5.1	8.0	1.2	2
Port Hueneme to Point Dume	1977	4	5.9	6.3	3.0	8.0	2.2	1
	1980	11	11	10	6.0	17	3.7	3
	1985	2	11		7.0	14	5.0	2
Newport to Dana Point	1977	3	11	10	8.3	15	3.5	1
	1978	6	15	16	9.5	19	3.2	4
	1985	1	17					2
Outfall Areas:								
Oxnard shelf	1971[a]	4	18	15	13	30	7.2	9
Santa Monica Bay	1970[a]	24	33	30	14	72	16	9
	1977[a]	13	26	19	7.7	92	23	1
	1978[b]	31	60	55	11	238	45	4
	1985[b]	3	26	26	25	27	1.0	5
Palos Verdes shelf	1970[a]	22	168	145	19	550	120	9
	1977[b]	8	283	260	8.6	782	263	1
	1978[b]	8	259	268	38	427	128	4
	1985[b]	10	206	166	36	529	153	5
Orange County shelf	1970[a]	24	33	30	14	72	16	9
	1977[b]	11	26	25	9.0	56	12	1
	1978[b]	12	20	18	9.4	31	6.4	4
	1985[b]	9	22	18	13	54	13	7
Point Loma shelf	1970[a]	5	22	19	16	36	8.2	9
	1977[b]	7	10	10	5.9	15	3.5	1
	1985[b]	8	22	18	9.0	68	19	8
Bays and Harbors:								
Marina del Rey[a]	1977	11	109	107	11	270	70	10
	1978	11	88	83	8.9	201	56	10
	1984	12	139	125	39	307	88	11
	1985	12	112	82	11	246	74	12
	1987	13	147	137	10	359	104	12
Los Angeles-Long Beach [a]	1973	31	110	88	18	339	74	14
	1978	31	103	89	18	233	68	15
Upper Newport Bay	1971	3	16	22	8	22	11	18
Upper Newport Bay[a]	1980	8	24	26	12	31	6.3	16
Lower Newport Bay	1971	7	160	46	20	7.3	248	18
Newport shipyards	1972	9	9488	6920	822	20300	6918	19
Newport shipyards	1981	9	592	580	236	10400	318	19
Newport shipyards	1986	6	610	550	310	830	198	19
San Diego Harbor[a]	1983	20	1235	143	18	19100	4229	17
San Diego Harbor	1974	11	476	231	138	1953	528	18
OVERALL					2.3	20300		

a - all depths; b - 60-m only

1 Word and Mearns,1979
2 Thompson et al. ,1987
3 Hershelman et al., 1983
4 Hershelman et al. 1980
5 Hyperion Treatment Plant, original data
6 CSDLAC, original data

7 CSDOC, original data
8 City of San Diego, original data
9 SCCWRP 1973; Galloway, 1972a & b
10 Soule and Oguri, 1980b
11 Soule and Oguri, 1985
12 Soule and Oguri, 1986

13 Soule and Oguri, 1987
14 Chen and Lu, 1974
15 Soule and Oguri, 1980a
16 MBC and SCCWRP, 1980
17 Ladd et al., 1984
18 Young et al., 1975
19 Liu and Schneider, 1988

Sediments in urban bays have been considerably more contaminated with copper than those in most coastal shelf areas. Ranking areas by most recent median sediment copper concentrations identifies four areas that may be judged "highly" contaminated (more than 10 times the coastal shelf "background" of 10 ppm dw; Table 7.2). These include areas in three embayments (Newport Bay shipyards in 1986, 55 times; San Diego Harbor in 1983, 14.3 times; and Marina del Rey in 1987, 13.7 times) and one coastal shelf site (Palos Verdes shelf at 60m in 1985; 16.6 times). Los Angeles-Long Beach harbors were the only "moderately" contaminated areas (between 3 and 10 times; 8.9 times in 1978). The only area with "slight" sediment copper contamination (up to 2 to 3 times background) was Santa Monica Bay in 1985 (2.6 times). The least copper-contaminated sediments were along the Santa Barbara shelf in 1985 and in the Tijuana Estuary in 1988 (as noted above).

Table 7.2. Median copper concentrations (ppm dw) in sediments and ratios to background reference concentrations for the most recent surveys in 3 shelf and bay regions.

Rank	Region	Year	Median
1	Newport shipyards	1986	550
2	Palos Verdes shelf	1985	166
3	San Diego Harbor	1983	143
4	Marina del Rey	1987	137
5	Los Angeles-Long Beach harbors	1978	89
6	Santa Monica Bay	1985	26
7	Orange County shelf	1985	18
8	Point Loma shelf	1985	18
9	Newport-Dana Point shelf	1985	17
10	Port Hueneme-Dume shelf	1985	11
11	Upper Newport Bay	1980	26
12	Santa Barbara shelf	1985	6.5
13	Tijuana Estuary [a]	1988	0.9, 2.3, and 12.7

[a] mouth, north, and south arms, respectively; Gersberg *et al.*, 1989

In the past, sediment copper concentrations have been much higher. The extreme case was at a suite of Newport Bay boatyard sites that, in 1972, had a median copper concentration of 6920 ppm dw (692 times above a possible reference value of 10 ppm dw).

The highest sediment copper concentrations resulting from the 1984-86 NOAA NS&T surveys occurred at a site in central San Diego Harbor, at Palos Verdes, and in outer Los Angeles Harbor near San Pedro (Figure 7.3). With the exception of one site off Palos Verdes, coastal shelf sites always contained lower copper concentrations than harbor sites.

In a national review of sediment effects data, Long and Morgan (1990) calculated a probable effects range (ER-L to ER-M) for copper of 70 to 390 ppm dw. However, sediments at Palos Verdes containing copper concentrations as high as 328 ppm dw were not toxic to the infaunal amphipod *Rhepoxynius abronius*; likewise, concentrations as high as 309 ppm dw were not associated with moderate or major degradation of marine infaunal communities at this site (Swartz *et al.*, 1986). The lower effects concentration (70 ppm) calculated by Long and Morgan (1990) was exceeded by median levels of copper in sediments from the Palos Verdes shelf, Marina del Rey, Los Angeles-Long Beach harbors, Newport Bay, and San Diego Harbor. The ER-M value was only exceeded at Newport Bay.

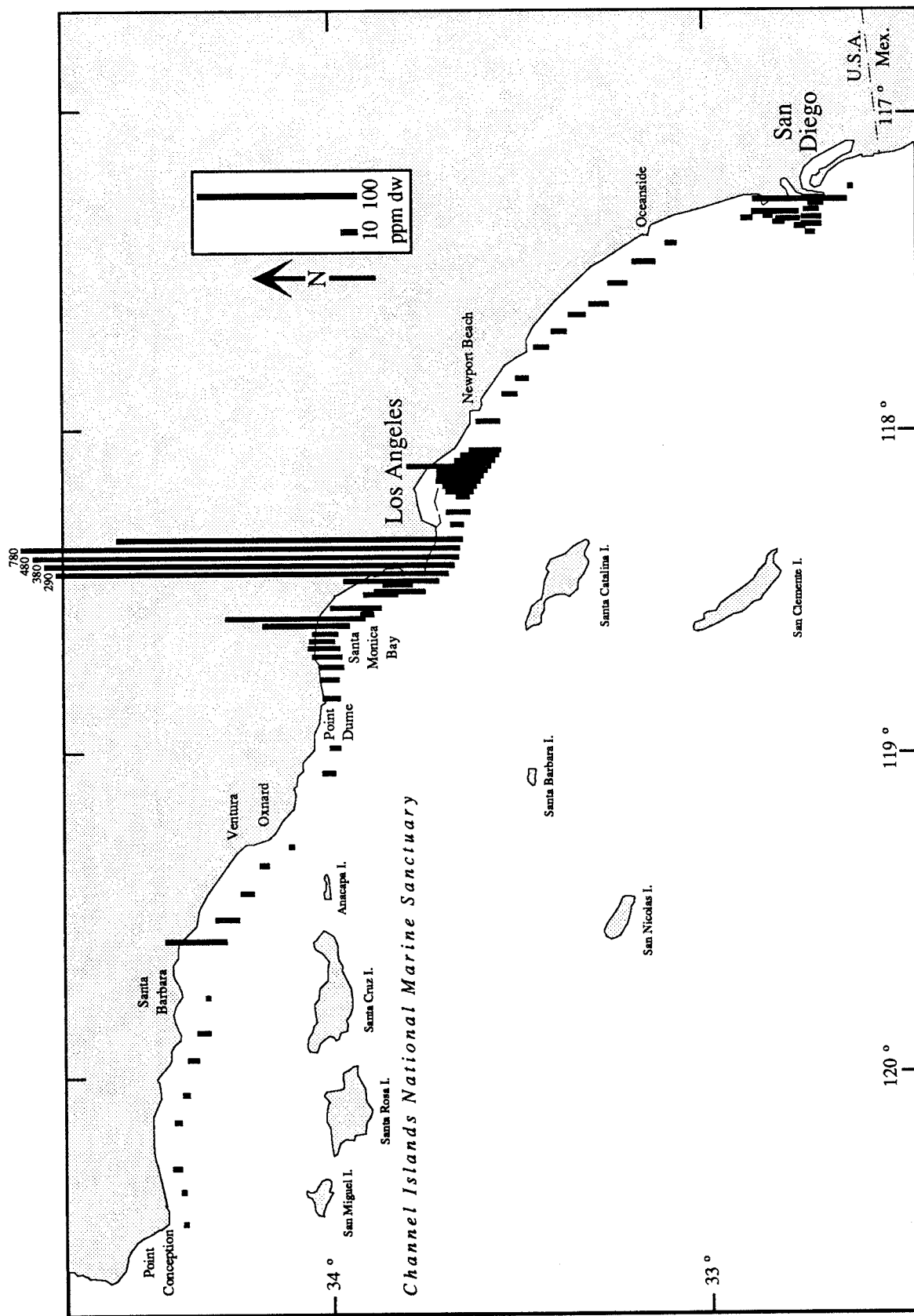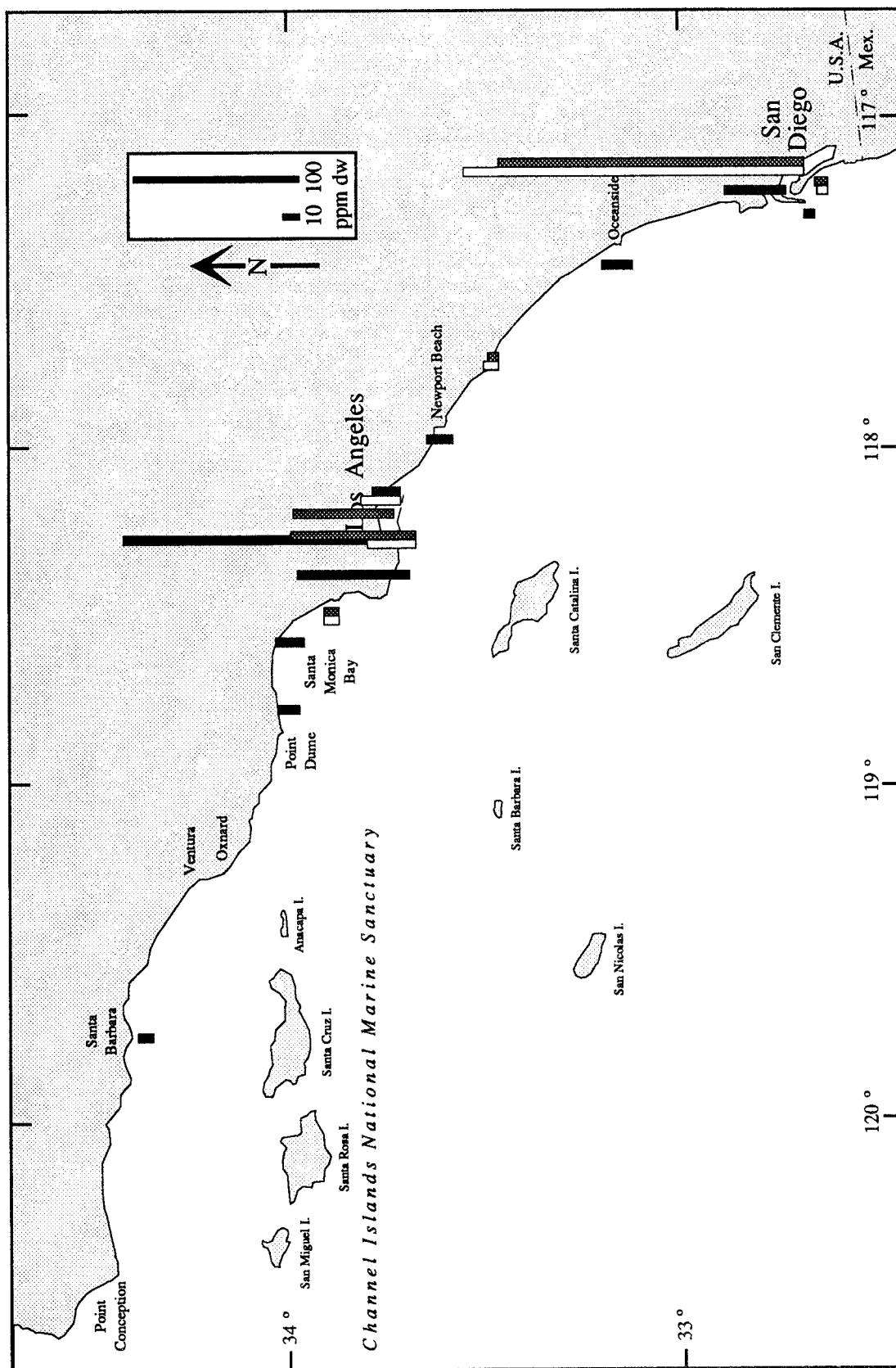**Figure 7.3. Copper concentrations in the surficial sediments of the Southern California Bight Based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 (▯) and 1985 (▮) and Mussel Watch Project for 1986 (▤) (NOAA, unpublished data and NOAA, 1988).**

Monitoring by CSDLAC in 1974 and 1980 (Stull and Baird, 1985) and in 1985 (CSDLAC, unpublished data) indicated that the mean concentrations along the 60-m isobath off Palos Verdes declined dramatically from over 575 ppm dw in 1974 to 206 ppm dw in 1985 (Figure 7.4). This reduction coincided with source control by CSDLAC (Stull *et al.*, 1988). Decreasing copper contamination was also reported for boatyard areas of Newport Bay between 1972 and 1980 (Liu and Schneider, 1988) and during the late 1970s near the Orange County outfall (CSDOC, 1976, 1977, 1978, 1980, and 1981).

Copper has been a regionwide anthropogenic contaminant of the northern and nearshore basins of the Bight since the early 1940s. In two basins (Santa Monica and San Pedro), copper concentrations and inputs doubled between 1960 and 1970 (inferred from Bruland *et al.*, 1974; Finney and Huh, 1989). In the Santa Barbara basin, copper increased only 25 percent during the same period (Bruland *et al.*, 1974) reaching a peak about 1970 and remaining virtually unchanged through the 1980s (Schmidt and Reimers, 1987). In the Santa Monica Basin, concentrations declined during the 1970s (Finney and Huh, 1989), consistent with observations at Palos Verdes (Stull and Baird, 1985) and with trends in emission rates (Stull *et al.*, 1988). Although peak contamination was in the 1960s on the Santa Monica shelf and basin, surface sediments (top 2 cm) are enriched with copper due to recycling and not due to current inputs (Finney and Huh, 1989).
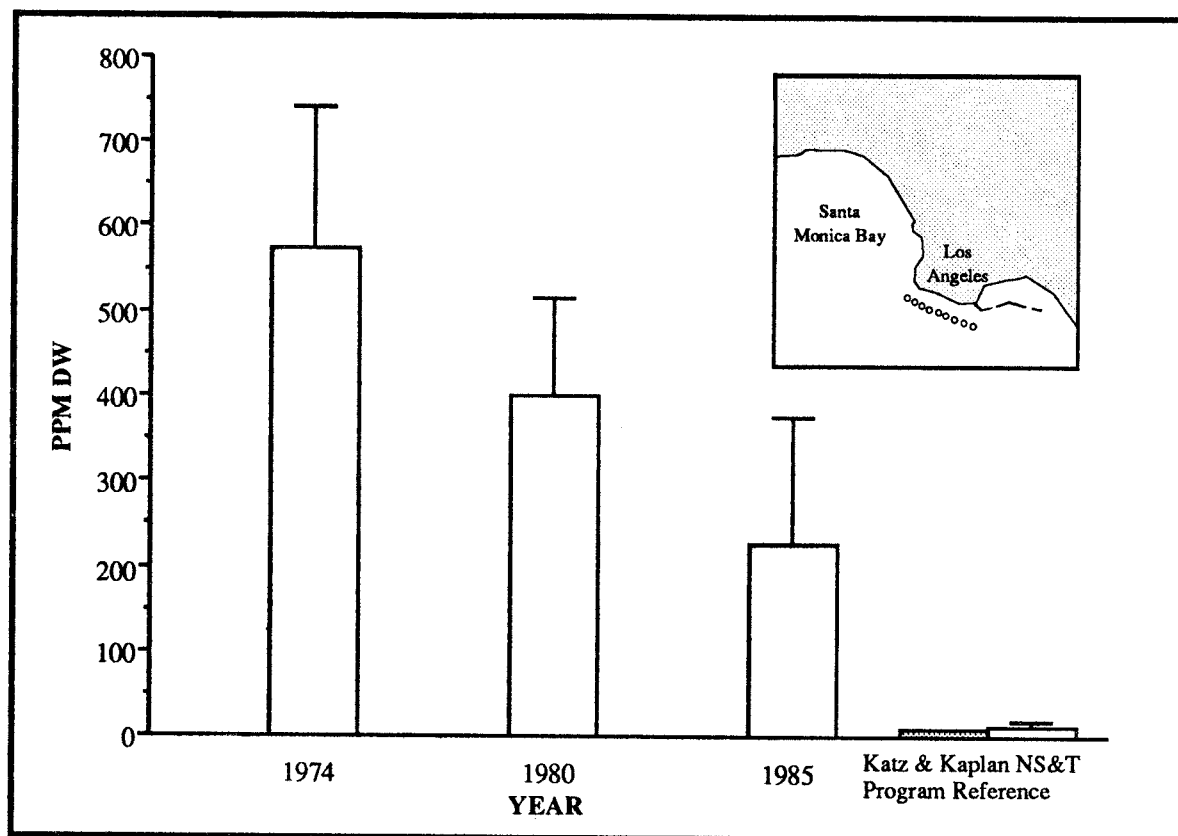
Figure 7.4. Mean copper concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC. The reference values are based on the value reported by Katz and Kaplan (1981) and the mean of four relatively isolated NOAA NS&TP sites in the Southern California Bight sampled between 1984 and 1986 (NOAA, 1988). Inset shows approximate locations of sites sampled by CSDLAC.

COPPER IN MUSSELS

In the Southern California Bight, the five data sets forming the basis for this discussion show many variabilities in levels of copper in mussels (*M. edulis* and *M. californianus*). Table 7.3 summarizes the ranges of results obtained in both species, as well as the location where the maximum concentration was measured. The highest concentration was 120 ppm dw from a 1985 CMW collection of *M. edulis* from inside Oceanside Harbor.

Although Eisler (1981) specifies proximity to anthropogenic point sources of copper as the primary determinant of molluskan tissue concentrations, results from the five surveys in the southern California region only partially reflect the impacts of some of the largest point sources: the municipal outfalls discharging into the coastal waters of the Bight. Alexander *et al.* (1976) attributed high copper concentrations in digestive gland of *M. californianus* collected in 1971 at Royal Palms and Point Loma (69 and 61 ppm dw, respectively; Figure 7.5) to adjacent wastewater inputs from Los Angeles and San Diego. However, this failed to explain elevated concentrations that occurred at Point Dume (42 ppm) and Santa Barbara Island (38 ppm); both removed from the immediate influences of municipal discharges. It is possible that coastal or offshore transport mechanisms may account for these and other values found in the survey (Figure 7.5).

Table 7.3. Summary results for copper in mussel tissue, Southern California Bight.

Study	Species	Tissue	Range (ppm dw)	Site with Maximum
1971 SCCWRP	*M. californianus*	Digestive gland	14-69	Royal Palms
1974 SCCWRP	*M. edulis*	Digestive gland	12.9-178	Inner Newport Bay
EPA Mussel Watch	*M. californianus*	Whole soft tissue	4.1-11	Palos Verdes-Point Fermin
	M. edulis	Whole soft tissue	6.1-11.2	San Diego Harbor
California Mussel Watch	*M. californianus*	Soft tissue less gonad	3.2-34.8	San Diego
	M. edulis	Soft tissue less gonad	4-120	Oceanside Harbor
NS&T Mussel Watch	*M. californianus*	Whole soft tissue	5.2-13	Point Loma
	M. edulis	Whole soft tissue	6.2-20	San Diego-Harbor Island

In 1974, the SCCWRP sponsored sampling and analysis of mussels in southern California harbor regions. The foci for this study were Los Angeles-Long Beach, San Diego, and Newport harbors; although other locations at Royal Palms, Seal Beach, La Jolla, and Point Loma were sampled as well. The first two harbors were chosen because of their heavy commercial and naval use, while Newport was selected because it represented a strictly recreational harbor with few known point-source inputs (Young *et al.*, 1979). Figure 7.6 shows mean concentrations of copper found in *M. edulis* during this survey. Young *et al.* attributed the highest concentrations, at Newport and San Diego harbors (the inner bay site in Newport Bay yielded a mean concentration of 130 ppm dw; the Shelter Island site in San Diego harbor, 73 ppm dw), to recreational and commercial vessel repainting and repair activities. The elevated value at Royal Palms (47 ppm dw) was linked to the JWPCP discharge directly offshore.
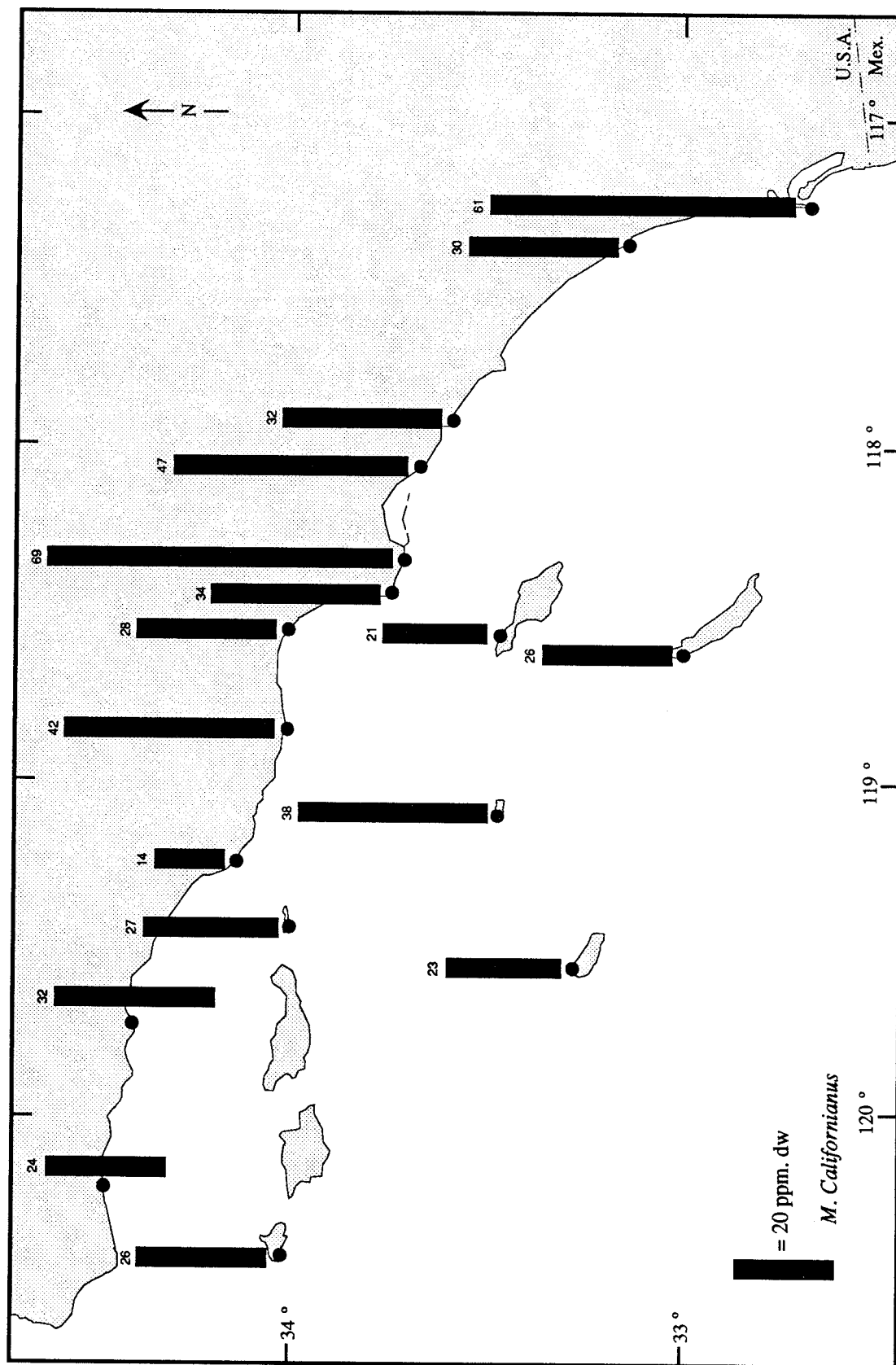
Figure 7.5. Copper in digestive gland of mussels, sampled in 1971. Values shown are means of six samples, each sample equals one individual.
Source: Young, 1974.
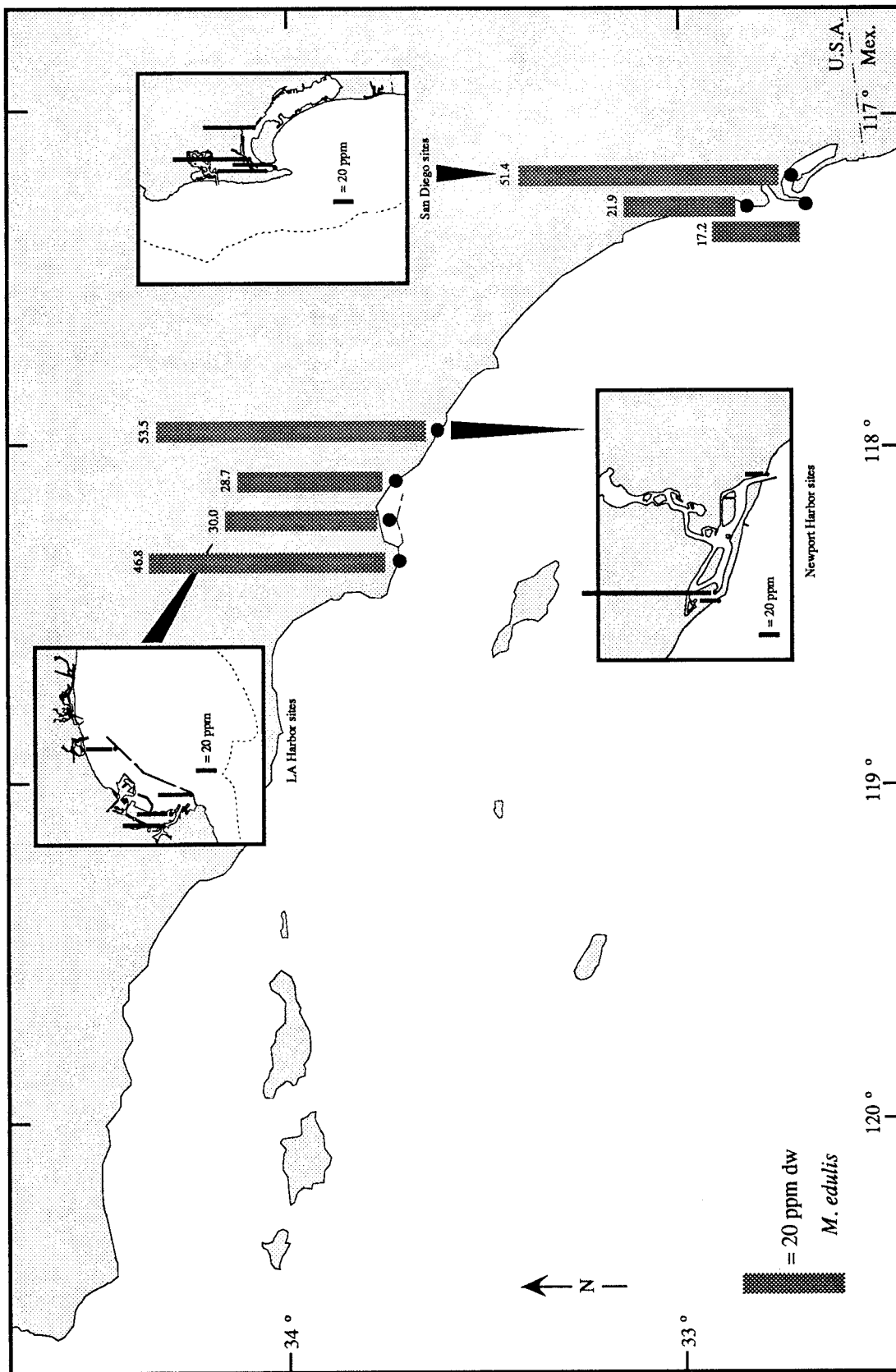
Figure 7.6. Copper in digestive gland of mussels sampled in 1974. Source: Young et al, 1979; Young, unpublished data.

The NS&T Mussel Watch Project examined 16 sites in the Southern California Bight in 1986. Results for levels of copper in tissue of *M. californianus* and *M. edulis* are shown in Figure 7.7. Although elevated concentrations in *M. edulis* were evident near commercial basins such as Los Angeles Harbor, San Diego Harbor, and in the heavily used recreational harbor at Marina del Rey, trends in *M. californianus* are less apparent. For example, the concentrations of 9.0 ppm and 11.0 ppm at Point Conception and Point Dume, respectively, are similar to that at the Royal Palms site (8.8 ppm), which was previously identified by Young *et al.* (1979) as being impacted by the JWPCP outfall located directly offshore. The surveys reviewed above provided evidence for localized copper contamination in mussels.

Copper concentrations in resident mussels have varied considerably within and among bays and harbors. Santa Monica had the highest average concentration (16.6 ppm dw; Figure 7.8) in *M. californianus* among three regions sampled in 1980 (Table 7.4); the mean and median were about 3 times higher than comparable values of 5.1 and 5.4 ppm dw at Santa Catalina Island and almost twice the average concentrations of a suite of 13 other coastal sites (Table 7.4). Based on more limited NOAA NS&T data from 1986, a site peripheral to Santa Monica Bay was also higher then than samples from offshore islands, the Santa Barbara coast, or other coastal *M. californianus* sites to the south (Table 7.4)

Table 7.4. Summary of copper concentrations (ppm dw) in whole *M. californianus* from various sampling areas in the Southern California Bight, 1980 and 1986, Phillips, 1988; NOAA, 1989.

Region or Site	Year	N	Mean	Median	Min	Max	SD	Source
Santa Monica Bay	1980	10	16.6	17.0	8.9	23.0	4.7	CMW
Catalina Island	1980	5	5.1	5.4	4.5	5.6	0.46	CMW
Newport to Imperial Beach	1980	13	9.4	8.0	6.3	19.0	3.9	CMW
Point Dume	1986	3r	11.0	11.0	10.0	12.0	–	NS&T
Santa Barbara and Channel Islands	1986	3	7.2	7.0	6.5	7.9	–	NS&T
Remaining NS&T coastal sites	1986	5	8.4	8.7	6.3	11.3	__	NS&T
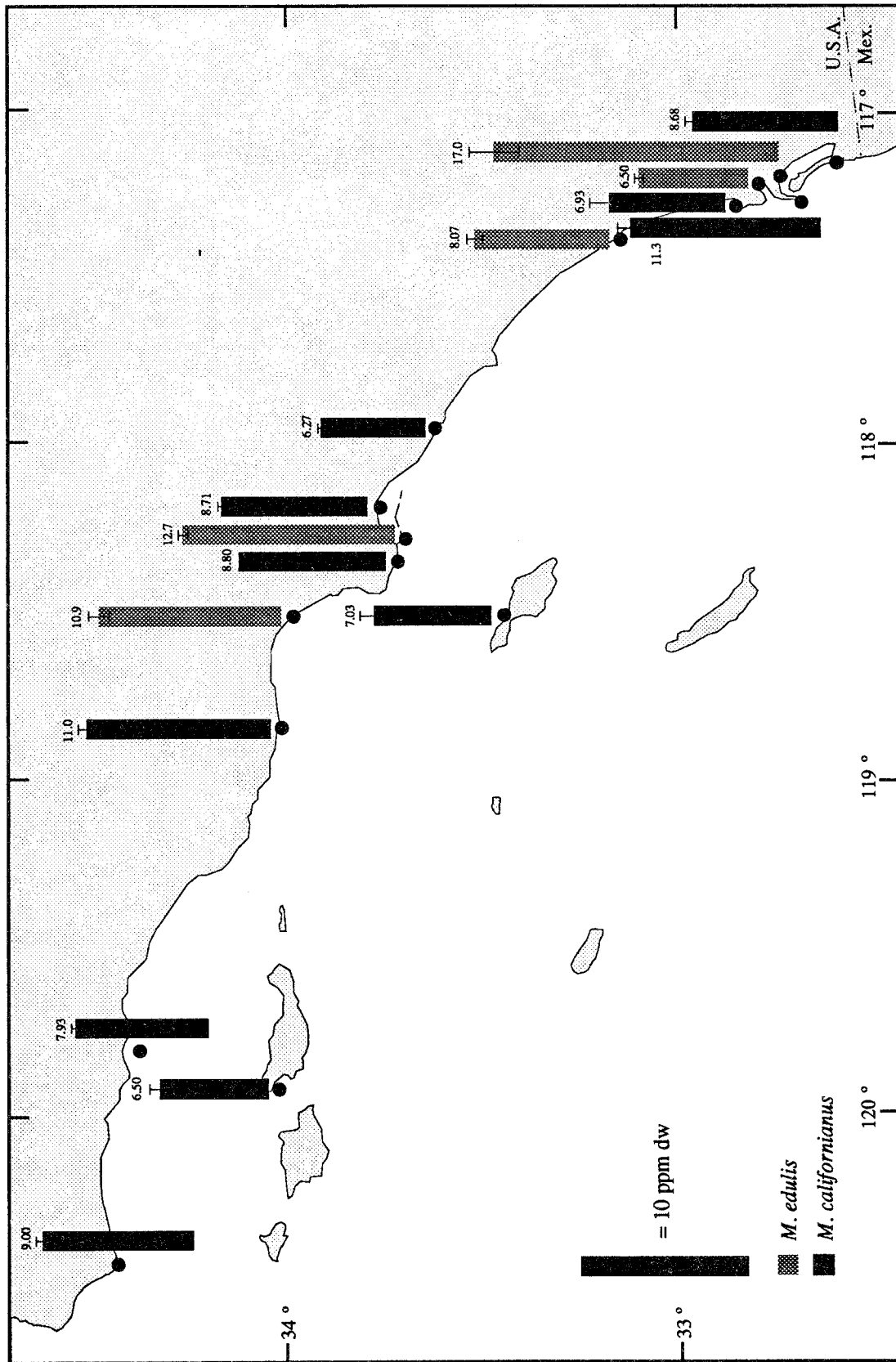
Figure 7.7. Copper in soft body tissue of whole mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

7-13
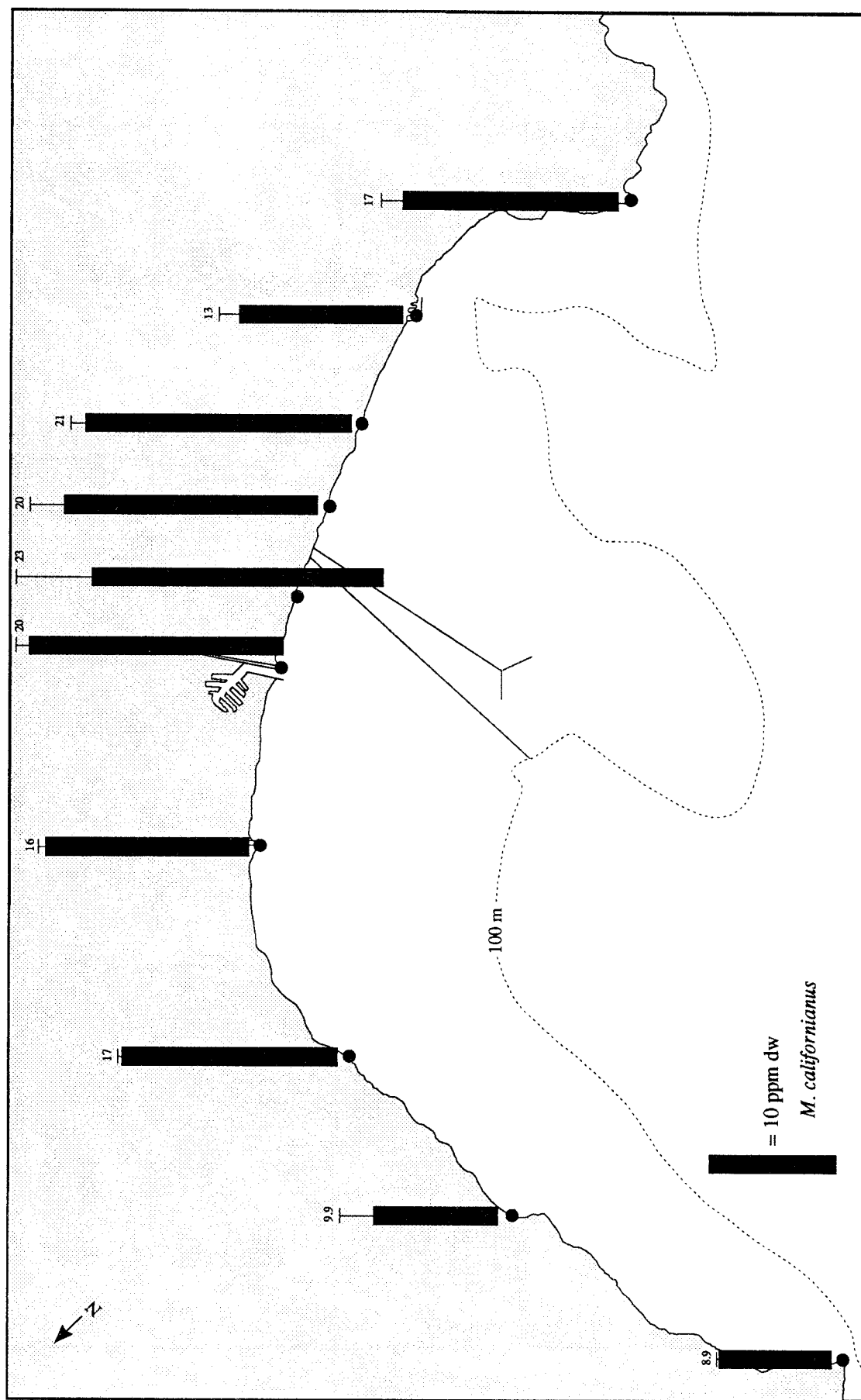
Figure 7.8. Copper in soft body tissue, less gonads, of whole mussels sampled in Santa Monica Bay in 1980. Source: Phillips, 1988.

= 10 ppm dw
M. californianus

100 m

N

7-14

Among other bays and harbors, Marina del Rey, San Diego Harbor, and Los Angeles-Long Beach harbors have produced *M. edulis* with high copper concentrations in the most recent years sampled (means of 26.4, 17.0, and 14.2 ppm dw respectively; Table 7.5). In Los Angeles-Long Beach harbors, the highest concentration occurred in *M. edulis* from Todd Shipyard in the inner harbor in 1984 (38.9 ppm dw).

Table 7.5. Summary of copper concentrations (ppm dw) in whole *M. edulis* from various sampling areas in the Southern California Bight, 1980 through 1986, Phillips, 1988; NOAA, 1989.

REGION OR SITE	Year	N	Mean	Median	Min	Max	SD	Source
Channel Islands Harbor (Oxnard)	1980	1	5.7	—	—	—	—	CMW
Marina del Rey	1980, 1982	2	26.4	26.4	13.0	39.7	—	CMW
Marina del Rey	1986	3r	10.9	11.0	9.6	12.0	—	NS&T
Los Angeles-Long Beach harbors	1980, 1985	17	14.2	12.0	7.2	38.9	7.5	CMW
San Pedro breakwater	1986	3r	12.78	12.0	12.0	13.0	—	NS&T
Colorado Lagoon (Long Beach)	1982, 1985	3	9.1	9.0	8.2	10.2	—	CMW
Anaheim Bay	1980, 1982	2	10.2	10.2	7.4	13.0	—	CMW
Newport Bay	1980, 1985	4	9.5	9.0	7.0	12.8	2.5	CMW
Newport Pier	1980	1	7.4	—	—	—	—	CMW
Oceanside Harbor	1985	1	120.0	—	—	—	—	CMW
Mission Bay	1980, 1982	5	6.7	6.6	4.0	8.8	1.8	CMW
Point Loma	1983	1	10.3	—	—	—	—	CMW
San Diego Harbor	1980, 1982	4	7.6	7.5	4.5	11.0	2.7	CMW
San Diego Harbor Island	1986	3r	17.0	17.0	14.0	20.0	—	NS&T

As noted above, the highest copper concentration recorded in the CMW program was 120 ppm dw from Oceanside Harbor. One obvious explanation for this high value was the application of copper sulfate by the harbor district to control algae.

Concentrations of copper in resident *M. edulis* from Newport Bay were low relative to the other harbors sampled (mean 9.5 ppm dw; Table 7.5). This situation is somewhat puzzling since Newport Bay has sites with extremely high copper contamination in sediments (see above). Compared to Marina del Rey, Los Angeles-Long-Beach harbors, or Oceanside Harbor, other bays and harbors have produced relatively low mean concentrations of copper in resident *M. edulis*. These include the Channel Islands Harbor near Oxnard (5.7 ppm dw), Colorado Lagoon in Long Beach (9.1 ppm dw), Anaheim Bay (10.2 ppm dw), and Mission Bay (6.7 ppm dw). It therefore appears that copper has been a contaminant in mussels principally of major recreational and industrial harbors, secondly in other harbors, and lastly along the coastal shelf.

Overall mean levels of copper for mussels sampled nationwide by NOAA's NS&T Program between 1986 and 1989 were similar to levels found at southern California sites. For all *M. californianus* sampled for NS&T, the mean level of copper was 8.745 ppm dw (median, 8.708 ppm dw). Levels of copper were higher in *M. edulis* (mean 12.215, median 10.433 ppm dw). The greatest range of copper values was found in *M. edulis* (3.267 to 300 ppm dw).

Results for copper in mussels from longer term monitoring at the Royal Palms site undertaken by the CMW Program, do not correlate well with mass emissions of copper reported for JWPCP discharges. Figure 7.9 illustrates that despite a substantial and generally steady decline in mass emissions of copper during the past decade, from 200 mt in 1976 to 33.5 mt in 1985, there has been no apparent corresponding decline in mussel tissue concentrations. Tissue levels of copper in *M. californianus* have remained essentially the same, within the range 6.8 to 10.5 ppm, between 1977 and 1985.

Although the EPA Mussel Watch Program only covered between 1976 and 1978, the results (Figure 7.10) resemble those of the CMW Program in that no discernible decline in *M. californianus* tissue concentrations of copper were noted at the site in closest proximity to the JWPCP outfall (Point Fermin). In fact, the EPA Mussel Watch results documented a slight increase each year, from 8.3 ppm dw in 1976, to 9.2 ppm in 1977, to 11 ppm in 1978, with co-occurring increases at Santa Catalina Island, Oceanside, and La Jolla.

There is some evidence to suggest that there may have been slight (2-fold) increases of copper in *M. californianus* on a regional basis. The ratio of mean copper concentration from five mainland coast sites and the mean for three island sites in the 1971 survey of metals in digestive glands was 1.8. In the 1977 CMW surveys of whole mussels (less gonads), the ratio at five comparable coastal and five island sites was 1.5. In the 1986 NOAA NS&T survey, the ratio at six comparable coastal and two island sites was 1.3. These ratios and their decline from 1.8 to 1.3 suggest there have been slightly higher levels of copper in mussels along the mainland coast than offshore and that these levels decreased between 1971 and 1986.

On the other hand, there is additional evidence pointing to a lack of long-term trends of copper at several sites monitored at least annually over the past decade. There is no statistically significant trend of copper in *M. californianus* over the period 1977-87 ($r^2 = 0.074$, p >>0.05). Nor was there a significant long-term trend at the CMW Oceanside jetty site ($r^2 = 0.004$, p >>0.05) or at an even more distant site north of the Bight, Montana de Oro State Park near Mono Bay ($r^2 = 0.039$, p>>0.05).

These results suggest that factors other than point source proximity may be responsible for copper body burdens in the Southern California Bight. Eisler (1981) notes that recognition of the importance of secondary biotic and abiotic modifiers is essential to understanding copper kinetics in marine systems, and these considerations may be of importance in determining the tissue concentrations observed in southern California mussels. Further, it may be the case that only certain tissues (such as the digestive gland used by Young *et al.*, 1974) accumulate copper. If so, metals in mussel digestive glands should be surveyed again.
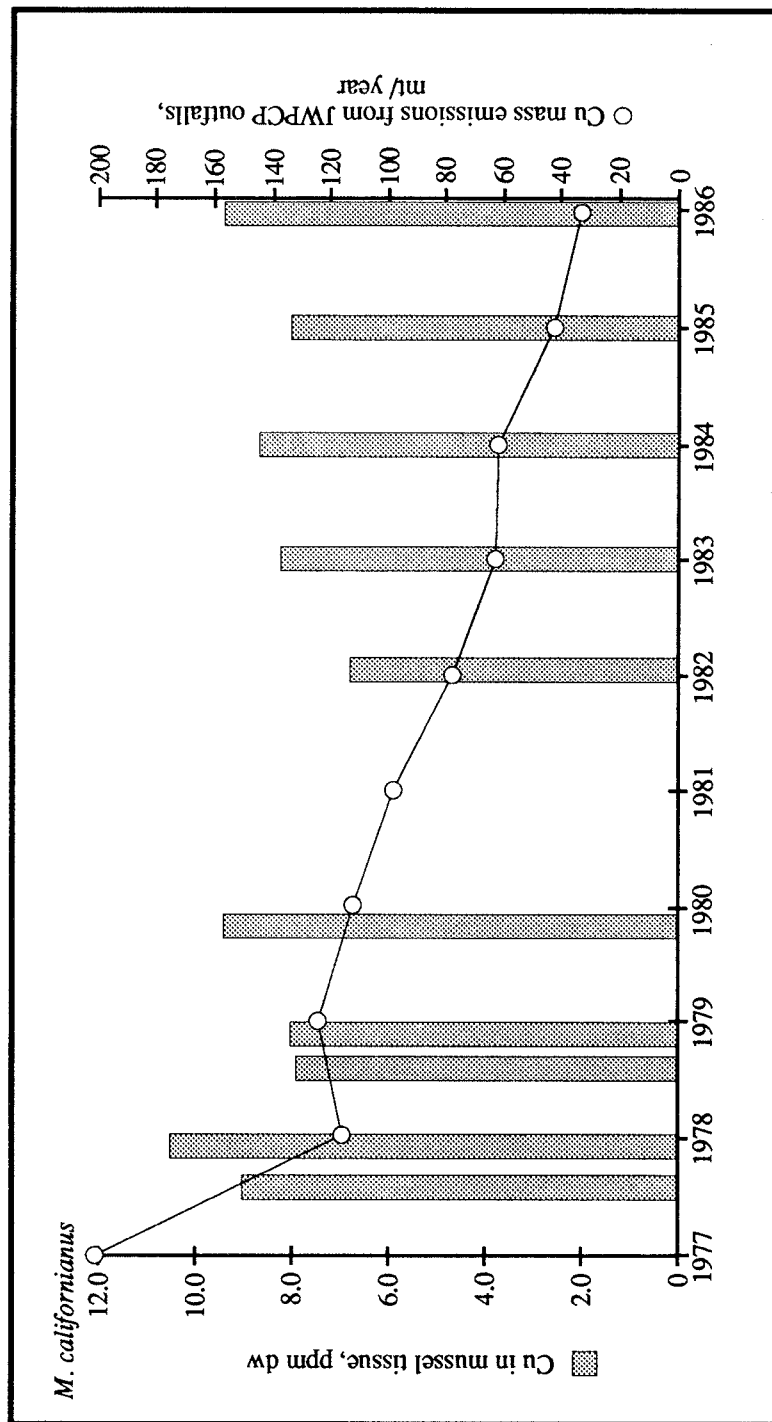
Figure 7.9. Comparison of JWPCP annual mass emissions of copper vs. concentrations of copper in tissue of mussels sampled at Royal Palms, 1977 through 1985. Sources: SCCWRP, 1987 and Phillips, 1988.
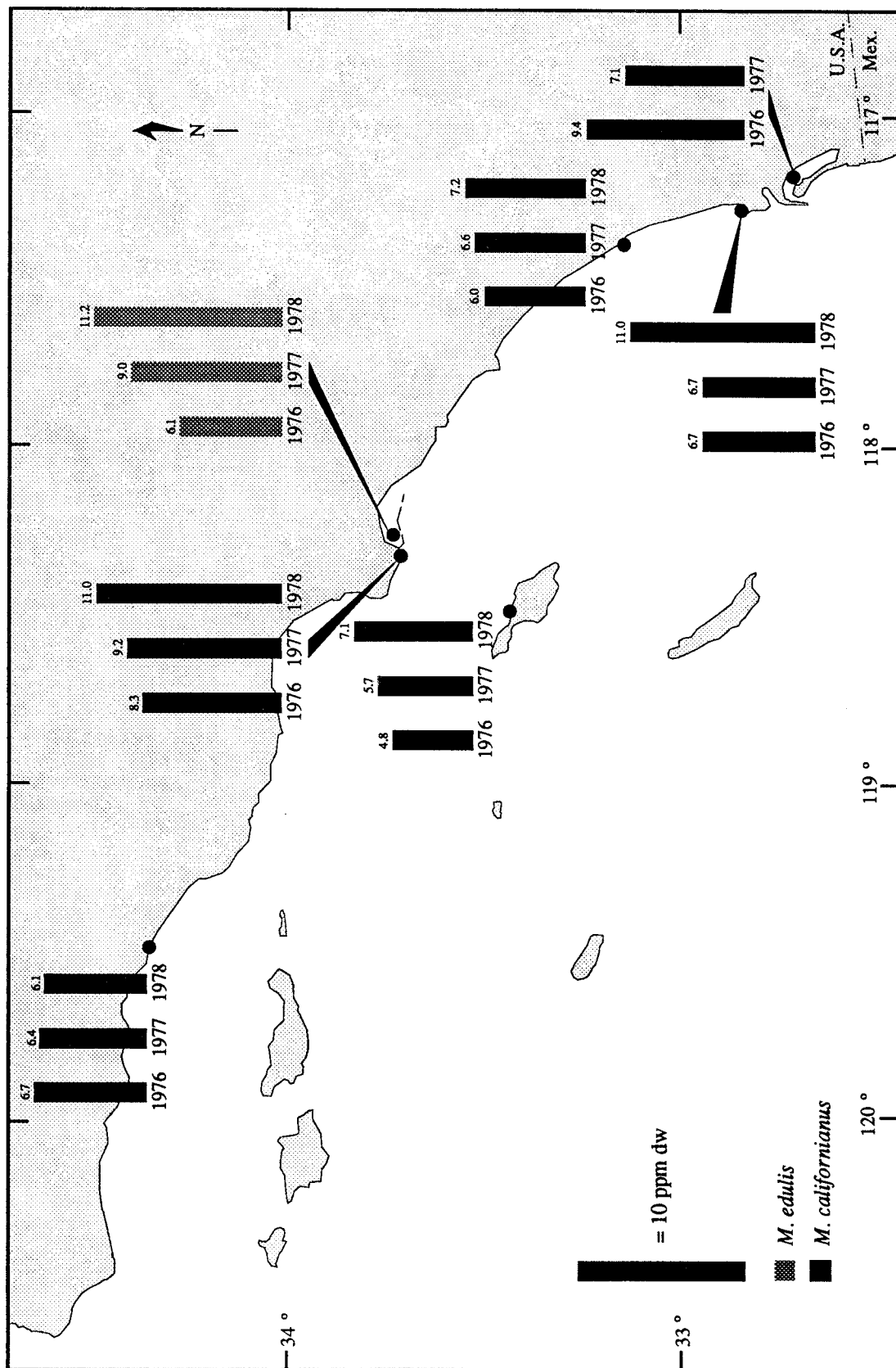
Figure 7.10. Copper in soft body tissue of whole mussels sampled in the Southern California Bight 1976-78. Source: EPA Mussel Watch Program.

COPPER IN FISH AND OTHER SPECIES

Copper has been analyzed in hundreds of samples of fishes and macroinvertebrates from the Southern California Bight.

Of 30 species from several studies selected from both nearshore and pelagic ecosystems, copper concentrations ranged from 0.2 ppm ww in a spiny dogfish from Palos Verdes, to 34.2 ppm ww in a spiny lobster collected in 1976 from Laguna Beach (Table 7.6). In general, higher concentrations occurred in muscle of macroinvertebrates (means, 0.14 ppm ww in purple-hinge scallop collected in 1973 near Santa Barbara to 34.2 ppm ww in California spiny lobster collected from Abalone Point, Laguna Beach, in 1976), and lower in muscle of fish (means, 0.09 ppm ww in California scorpionfish from Orange County in 1974-76 and 0.63 ppm ww in northern anchovy from Los Angeles Harbor in 1980) and sharks (means, 0.10 in spiny dogfish from Palos Verdes to 0.29 in a white shark (*Carcharodon carcharias*) from Santa Catalina Island). These patterns led Young *et al.* (1980) and Young *et al.* (1987) to conclude that copper does not undergo biomagnification in marine food webs of the Southern California Bight.

In a special 1975-77 study of contaminants in popular seafood organisms, Young *et al.* (1978; 1981a) concluded that copper was slightly elevated in three species, depressed in three others, and unaffected in six others collected near two outfall sites (Palos Verdes and/or Orange County) relative to specimens from control or reference areas.

De Goeij *et al.* (1974) observed a lack of bioaccumulation of copper in livers of Dover sole collected in 1971-72 near highly copper-contaminated sediments at Palos Verdes relative to fish from other island and coastal reference sites. For example, concentrations in fish from the central Palos Verdes Peninsula ranged from 1.65 to 2.65 ppm ww compared to 1.7 to 2.7 ppm ww in fish from Santa Catalina Island. However, livers of fish from areas adjacent to Palos Verdes with less contaminated sediments did have elevated copper levels (2.8 to 3.2 ppm ww in southern Santa Monica Bay and 3.05 to 6.8 in northern San Pedro Bay; Figure 7.11). Comparable data were obtained from a test and reference site sampled in 1988 near the Pacific Baroness wreck 12 miles south of Point Conception. Livers of Dover sole from the wreck site had a median copper concentration of 1.4 ppm ww while a median of 2.6 ppm was measured in livers of 10 Dover sole from a reference site (Dr. Stanley Margolis, University of California, Davis, personal communication, 1989). These results also partially agree with data collected during the NOAA NS&T 1984 Benthic Surveillance Project (Figure 7.12). In hornyhead turbot, liver copper concentrations were high at San Pedro Canyon relative to Santa Monica Bay, Dana Point, and San Diego Bay (Figure 7.12). In barred sand bass, concentrations were similar at Dana Point and in San Diego Bay (Figure 7.12); but, in white croaker, liver copper values were nearly 3 times higher in fish from the Dana Point "reference" site than in fish from the presumably more contaminated Seal Beach site near Long Beach (Figure 7.12).

There are no U.S. standards or action limits for copper in seafood organisms. However, six nations in a review by Nauen (1983) have criteria that range from 10 to 30 ppm ww (median 20 ppm). Muscle of all southern California fish reviewed in Table 7.6 contain copper at levels 10 percent or less of the minimum criteria of 10 ppm ww. Likewise, no fish exceeded the maximum of 30. However, spiny lobster collected from Laguna Beach in 1975-77 exceeded the maximum; and several invertebrate species from Palos Verdes (also 1975-77) exceeded the median of 20 ppm ww.

Table 7.6. Copper in edible tissues of marine organisms (ppm ww) from the Southern California Bight

| Common Name	Site	Year	No. of Samples	Mean	Median	Min	Max	Standard Deviation	Source
Giant kelp	Los Angeles Harbor	1980	5	0.52	0.53	0.47	0.60	0.05	Young and Mearns, 1980
Mysids (whole)	Palos Verdes	1981	8	4.56	5.04	1.61	6.84	1.88	Young and Mearns, 1980
Zooplankton (whole)	Coastal	1980-81	5	1.12	0.98	0.61	2.25	0.67	Schafer et al., 1982
Black Abalone	Santa Catalina Island	1975-77	3	3.59	4.11	1.97	4.68	1.43	Young et al, 1978
	Dana Point	1975	4	5.14	5.10	3.48	6.88	1.66	Young et al, 1978
	San Clemente	1975	7	4.15	3.30	1.61	9.35	2.73	Young et al, 1978
	Whites Point	1976	5	3.11	3.35	1.78	4.38	1.04	Young et al, 1978
Gaper Clams	Los Angeles Harbor	1980	5	0.63	0.50	0.44	1.03	0.25	Young and Mearns, 1980
Market Squid	Coastal	1980-81	3	15.77	14.20	11.50	21.60	5.23	Schafer et al, 1982
Purple-hinge Scallop	Palos Verdes	1976	8	0.23	0.24	0.08	0.33	0.09	Young et al, 1978
	Santa Barbara	1973	2	0.14	-	0.12	0.16	0.03	Young et al, 1978
	Santa Catalina Island	1973-74	4	0.17	0.11	0.09	0.36	0.13	Young et al, 1978
	Laguna	1975	9	0.19	0.14	0.09	0.48	0.12	Young et al, 1978
	Dana Point	1976	1	0.29	-	-	-	-	Young et al, 1978
California Spiny Lobster	Cortez Bank	1975	1	14.90	-	-	-	-	Young et al, 1978
	San Diego	1977	3	5.80	6.40	4.56	6.43	1.07	Young et al, 1978
	Santa Catalina Island	1976	9	16.69	12.90	9.04	26.80	6.99	Young et al, 1978
	Point Dume	1976	2	4.75	-	2.42	7.07	3.29	Young et al, 1978
	Palos Verdes	1976	5	9.10	8.73	3.26	15.08	4.87	Young et al, 1978
	Palos Verdes	1976	1	34.20	-	-	-	-	Young et al, 1978
Ridgeback Prawn	Palos Verdes (west)	1976	3	1.94	1.97	1.56	2.28	0.36	Young et al, 1978
	Orange County	1975-76	3	9.61	9.54	2.22	14.10	3.40	Young et al, 1978
	Palos Verdes	1980	5	5.49	5.35	4.12	7.22	1.18	Shafer et al, 1982
	Santa Catalina Island	1976	10	8.38	8.21	3.38	13.10	3.28	Young et al, 1978
Yellow Crab	Palos Verdes	1975-76	9	6.90	6.72	2.18	15.60	4.57	Young et al, 1978
	Dana Point	1976	3	10.70	13.10	3.60	15.40	6.26	Young et al, 1978
	Orange County	1975	3	8.50	10.00	1.50	14.00	6.38	Young et al, 1978
Bocaccio	San Clemente Island	1977	3	0.18	0.13	0.12	0.29	0.09	Young et al, 1978
	Palos Verdes	1973	1	0.13	-	-	-	-	Young et al, 1978
	Orange County	1975-79	7	0.17	0.17	0.07	0.34	0.09	Young et al, 1978
California Halibut	Los Angeles Harbor	1980	4	0.19	0.15	0.13	0.34	0.10	Young and Mearns, 1980
	Ventura County	1976	2	0.12	-	0.04	0.19	0.10	Young et al, 1978
	Palos Verdes	1976	4	0.11	0.09	0.05	0.21	0.07	Young et al, 1978
	San Diego	1976	2	0.14	-	0.11	0.17	0.04	Young et al, 1978
California Scorpionfish	Palos Verdes	1974-76	9	0.28	0.18	0.05	0.85	0.25	Young et al, 1978
	Orange County	1974-76	10	0.09	0.09	0.02	0.23	0.06	Young et al, 1978
	Dana Point	1976	5	0.14	0.15	0.10	0.18	0.03	Young et al, 1978
	Palos Verdes	1980	4	0.19	0.18	0.15	0.26	0.05	Shafer et al, 1982
	Santa Catalina Island	1974-75	3	0.20	0.11	0.10	0.40	0.17	Young et al, 1978
Dover Sole	Palos Verdes	1980	5	0.18	0.15	0.11	0.31	0.08	Schafer et al, 1982
Pacific Sanddab	Palos Verdes	1975	10	0.26	0.22	0.13	0.62	0.14	Young et al, 1978
	Catalina Island	1973	3	0.21	0.17	0.09	0.37	0.14	Young et al, 1978
Northern Anchovy	Los Angeles Harbor	1980	5	0.63	0.61	0.49	0.78	0.12	Young and Mearns, 1980
	Coastal	1980-81	5	0.39	0.34	0.25	0.64	0.15	Shafer et al, 1982
Pacific Bonito	Coastal	1980-81	5	0.48	0.34	0.29	1.12	0.36	Schafer et al, 1982
Pacific Hake	Coastal	1980-81	5	0.20	0.21	0.13	0.31	0.07	Schafer et al, 1982
Pacific Mackerel	Coastal	1980-81	6	0.37	0.39	0.17	0.65	0.17	Schafer et al, 1982
Pacific Sardine	Coastal	1980-81	5	0.33	0.25	0.22	0.62	0.17	Schafer et al, 1982
Spotted Sand Bass	Newport Bay	1978	3	0.23	0.26	0.16	0.26	0.06	MBC and SCCWRP, 1980
Striped Bass	Newport Bay	1978	3	0.27	0.27	0.24	0.29	0.02	MBC and SCCWRP, 1980
Striped Mullet (adult)	Newport Bay	1978	3	0.57	0.55	0.30	0.85	0.28	MBC and SCCWRP, 1980
Striped Mullet (Juvenile)	Newport Bay	1978	3	0.26	0.24	0.18	0.36	0.09	MBC and SCCWRP, 1980
Swordfish	Coastal	1980	5	0.35	0.31	0.13	0.60	0.17	Schafer et al, 1982
Topsmelt	Newport Bay	1978	3	0.19	0.20	0.13	0.23	0.05	MBC and SCCWRP, 1980
White Croaker	Palos Verdes	1975-77	9	0.27	0.26	0.11	0.55	0.14	Young et al, 1978
	Orange County	1975-77	10	0.27	0.15	0.02	1.14	0.33	Young et al, 1978
	Dana Point	1975-77	5	0.13	0.11	0.10	0.19	0.04	Young et al, 1978
	Los Angeles Harbor	1980	5	0.45	0.50	0.29	0.55	0.12	Young and Mearns, 1980
	Palos Verdes	1980	5	0.24	0.25	0.19	0.29	0.04	Schafer et al, 1982
Yellowfin Croaker	Newport Bay	1978	3	0.30	0.26	0.23	0.42	0.10	MBC and SCCWRP, 1980
Spiny Dogfish	Palos Verdes	1980	5	0.10	0.11	0.02	0.19	0.07	Schafer et al, 1982
Thresher Shark	Coastal	1980-81	5	0.27	0.27	0.10	0.40	0.12	Schafer et al, 1982
Mako Shark	Coastal	1980	5	0.27	0.32	0.10	0.34	0.10	Schafer et al, 1982
White Shark	Santa Catalina Island	1980-81	3	0.29	0.24	0.16	0.47	0.16	Schafer et al, 1982
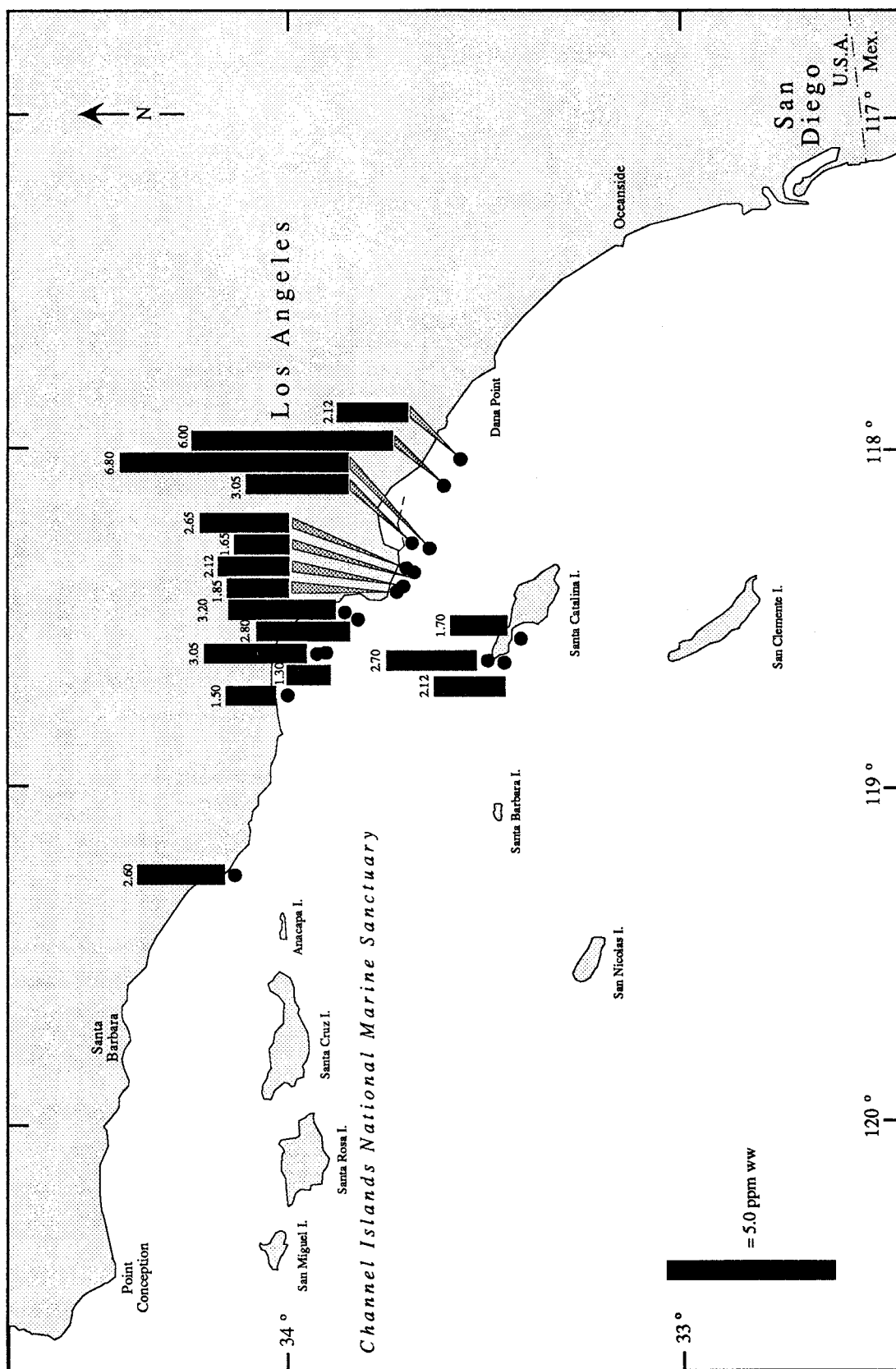
Figure 7.11. Copper concentrations (ppm ww) in liver tissue of Dover sole collected in the Southern California Bight in 1971-72. Source: de Goeij et al. (unpublished).
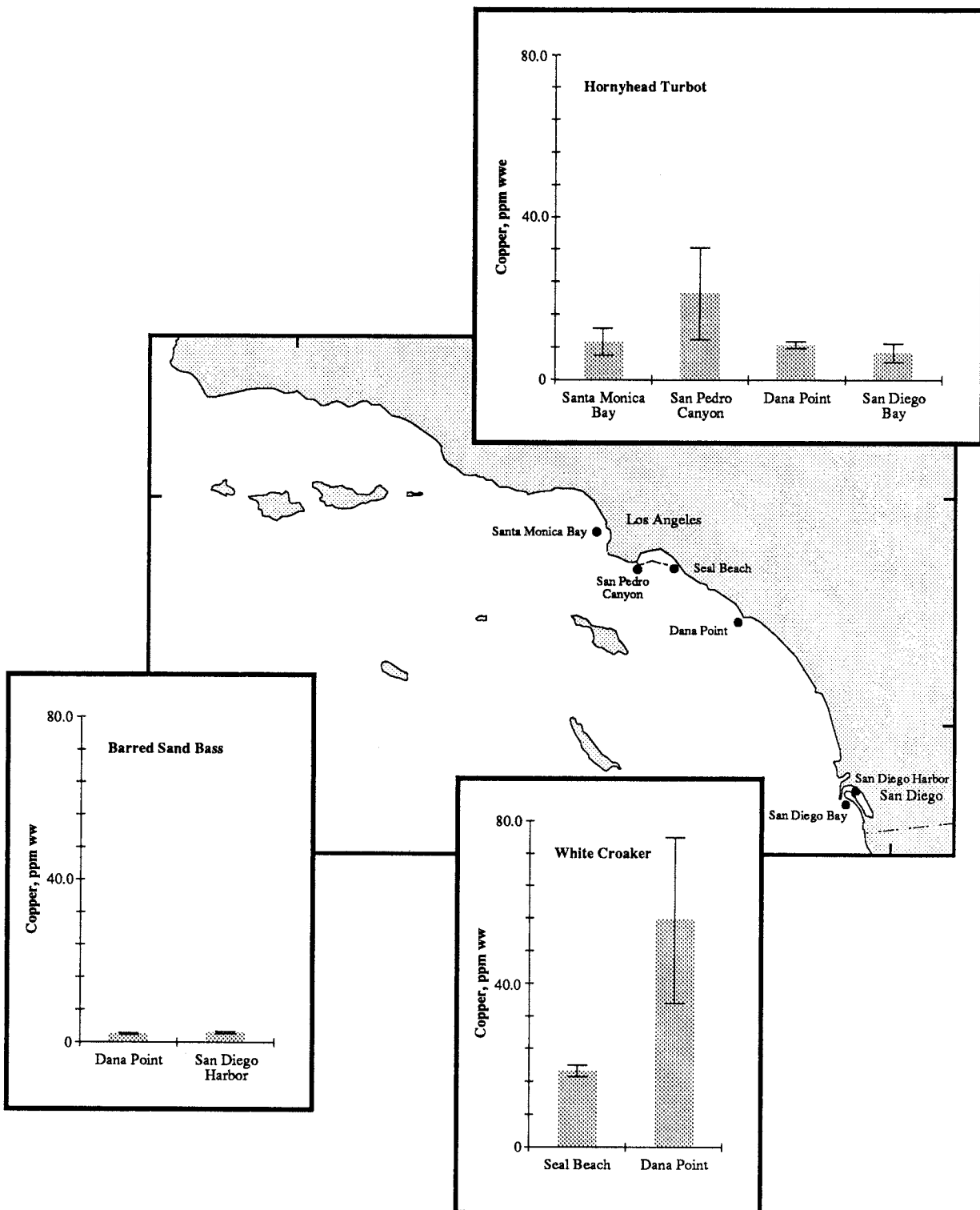
Figure 7.12. Concentrations of copper measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

SUMMARY AND CONCLUSIONS

Coastal, harbor, and bay sediments of the Southern California Bight have experienced a 7,800-fold range of copper concentrations. With the exception of Palos Verdes, the highest levels of copper in sediments were in harbors. Most coastal shelf areas have been free of copper contamination. Ore spillage was a source at one site in San Diego Harbor; but, it is clear from surveys in Newport Bay that vessel activities and boatyards have been locally dominant sources. The overall copper contamination of harbor sediments is consistent with historical use of copper-based vessel coatings. Nevertheless, site specific source control actions in municipal wastewater and in boatyard activities have lead to substantial local decreases in sediment copper contamination. It may be important to maintain surveillance of sediment copper since it is being considered as a replacement for the tributyl tin antifouling coatings used in the past.

Despite the dramatic ranges of copper in sediments of the Bight, there has been little indication of large-scale contamination of mussels by copper. Even though concentrations at Palos Verdes were elevated above other coastal sites, they did not decline with source control or with declining concentrations in offshore sediments. Further, while inputs from sewage were declining in the late 1970s; levels in mussels from several areas were increasing. These observations suggest copper in coastal mussels has been controlled by factors other than sewage inputs. It is possible that copper in coastal mussels from sites such as Royal Palms on the Palos Verdes Peninsula, is influenced by copper from adjacent harbors. Locally (within harbors) there have been sites with high levels of copper in mussels that, to some extent, reflect levels in nearby sediments.

Copper has not contaminated fish and most other species in any regionwide pattern that reflects proximity to outfalls or to contaminated sediments. Further, copper does not undergo biomagnification in coastal food webs of the Bight; it decreases in concentration with trophic level. Finally, ambient levels in edible tissues of fish have not exceeded the lowest known international criteria, although those in some shellfish species have.

INFORMATION NEEDS

Monitoring should be resumed or initiated to track the direction and magnitude of trends in copper concentrations in sediments, mussels, and several other shellfish species from Palos Verdes and in sediments and mussels from Los Angeles-Long Beach harbors, Newport Bay (near shipyards), and San Diego Harbor. Copper concentrations in livers of previously sampled fish species from the Los Angeles coastal area should be re-surveyed to determine if depressed levels still exist. Finally, trends in vessel paint formulations should be tracked. If application of copper-based formulas increase, monitoring of copper in harbors and marinas may need to be increased.

CHAPTER 8

LEAD

Lead, which has no necessary biological function and is toxic to most organisms at high concentrations, causes a number of acute and chronic human health impacts. These include effects on the nervous, circulatory, renal, and excretory systems and on reproduction and carcinogenesis. A serious impact is related to the central nervous system (Goyer, 1986). Lead is considered to be a contaminant of primary concern because of its widely described toxicological effects, its many industrial uses, and its occurrence in the natural environment and in anthropogenic waste materials. Arnold and Farrow (1987) list lead as a pollutant constituent in over 50 general categories of industrial process wastewater discharges. Eisler (1988b) stresses the role of spent lead shot and lost fishing sinkers as sources of lead leading to death of wildfowl.

The largest human source of lead to the environment is a nonpoint, or nondiscrete, source: that originating from the use of tetraethyl lead as a gasoline additive. In 1972, before the availability of unleaded gasoline, the Los Angeles region consumed an estimated 24 mt of lead fuel additives each day (Huntzicker et al., 1975). If 30 to 90 percent of the lead content in this gasoline entered the air with automobile exhaust (Provenzano, 1978), then 7 to 22 mt of lead were dispersed into the region daily. This agrees with the estimate of Huntzicker et al. (1975) of 17.6 tons per day. On a worldwide scale, Nriagu (1978) estimated that 267,000 (61%) of the total 438,000 mt of lead released per year from anthropogenic sources in the mid 1970s derived from anti-knock additives. This exceeded the next largest source type (iron and steel production) by more than a factor of 5. This global release was equivalent to 731 mt per day. This means that the daily release in the Los Angeles Basin was over 3 percent of the daily lead release to the global atmosphere.

Locally significant amounts of lead are also discharged directly into the marine environment by sewage treatment plants and industrial operations. SCCWRP (1973) estimated that of 1339 mt of non-advective (non-ocean current) lead entering the Bight in 1971, 74 percent (1,000 mt) came from direct rainfall, 16 percent (211 mt) from wastewater discharges, 7 percent (28 mt) from surface run-off, 2 percent from ocean dumping, and less than 1 percent (10 mt) from vessel antifouling paints. Since then, emissions from sewage have decreased from the range of 152 to 243 mt per year during the period 1971-79 to 94 to 120 mt per year during the period 1983-85 (SCCWRP, 1987A) and to 64 mt in 1987 (SCCWRP, 1988; Figure 8.1). Meanwhile, Schafer and Gossett (1988) reported that run-off from the Los Angeles River alone varied from 64 mt in 1971-72, to 108 mt in 1979-80, and 32 mt in 1985-86. Inputs from lost fishing weights and sinkers and lead shot have not been estimated.
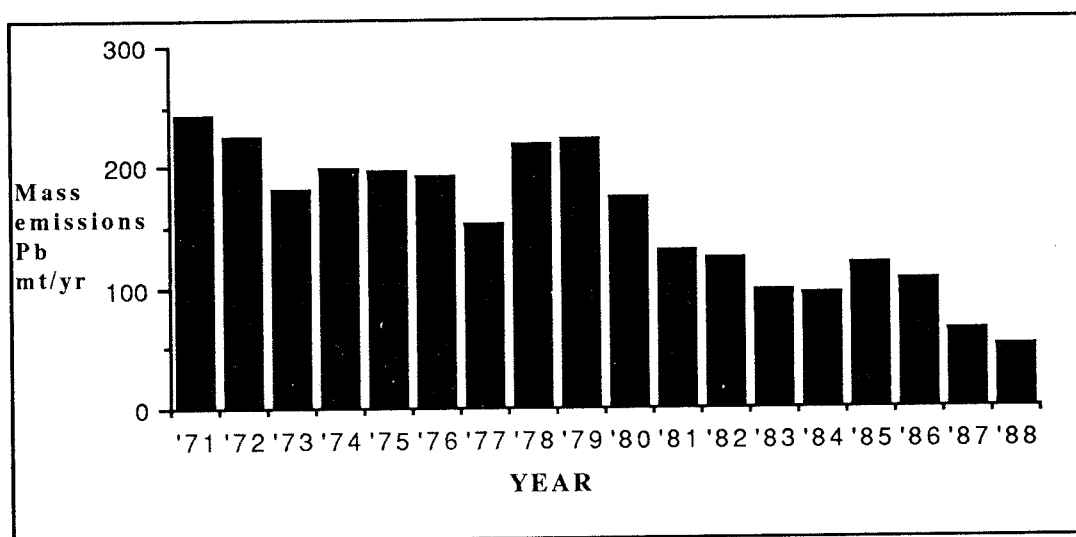

Figure 8.1. Combined annual mass emissions of lead for seven southern California dischargers, 1971-88. Source: SCCWRP, 1989.

LEAD IN SEDIMENTS

Like many other trace elements, lead has been measured in thousands of samples of sediments throughout the Bight. In the synoptic coastal, bay, and harbor surveys selected for this review, lead concentrations in surface sediments ranged from 1.0 ppm dw at a site in inner Bolsa Bay sampled in 1978 to 4400 ppm dw in San Diego Harbor in 1973 (Table 8.1).

Bays and harbors of southern California had average lead concentrations up to 5 times higher than adjacent coastal shelf areas. Median mainland shelf sediment concentrations at sites remote from major urban areas have been in the range of 4 to 10 ppm dw. Individual concentrations ranged from 2.4 at a site on the Santa Barbara shelf to 29 ppm dw at a 60-m site between Point Dume and Port Hueneme (Table 8.1). In contrast, median concentrations in bays and harbors have ranged from 8 to 994 ppm dw.

Using data from the SCCWRP 1977 60-meter survey, Katz and Kaplan (1981) judged the shelf background lead concentration to be about 10.5 ppm dw. Concentrations at the bottom of cores from both shelf and basin areas ranged from 8 to 18 ppm dw with an average of 9.5 (Katz and Kaplan, 1981). Christensen et al. (1978) estimated that background lead concentrations in Upper Newport Bay were about 10 ppm dw before a documented rise beginning in 1955. Thus, three independent surveys suggest a background lead concentration of 10 ppm dw. However, lead concentrations do vary with depth and other factors on the coastal shelf. Over the depth range of 15 to 745 m along the Ventura-Los Angeles County coast between Point Mugu and Point Dume, Hershelman et al. (1982) reported significant ($p \leq .01$) increases with depth ($r^2 = 0.451$) and total volatile solids ($r^2 = 0.510$); and decreases with percent solids ($r^2 = -0.482$). However, the increase with depth was not linear and the average concentration increased from 4.7 ppm dw in shallow water (14 to 30 m) to 15.3 ppm dw on the slope (260 to 360 m) then decreased to 8.7 ppm dw in the basin (713 to 745 m). Thus, a baseline of 10 ppm dw is midway between average shallow and average slope concentrations along this relatively unpopulated part of the coast.

The overall national mean concentration of lead in sediment at sites sampled by NOAA's NS&T Program between 1984 and 1989 is higher than the 10 ppm dw background level calculated by Katz and Kaplan (1981). The mean level of lead from all sites was 30.078 ppm dw (median, 18.957 ppm dw). Site means ranged from below detection limits to 196.67 ppm dw.

Assuming a background of 10 ppm dw, two recently sampled areas stand out with very high concentrations (more than 10 times background): the Newport Bay shipyards in 1986 (median 140 ppm dw or 14 times background) and Marina del Rey (median 120 ppm or 12 times background; Table 8.2). Six areas had high median concentrations (3 to 10 times background): Huntington Harbor (9.2 times), Santa Monica Bay (8.8 times), San Diego Harbor (8.4 times), the Palos Verdes shelf (6.9 times), Inner Bolsa Bay (5.2 times), and Outer Bolsa Bay (4.2 times). Five other areas were slightly contaminated (with median concentrations of up to 3 times background): Dana Harbor (2.4 times), Upper Newport Bay (2.3 times), the south arm of the Tijuana Estuary (2.0 times), the Point Loma shelf (1.9 times), and the Los Angeles-Long Beach harbors (1.7 times). The coastal shelf areas between Santa Barbara and Point Dume and between Newport and Dana Point had lead concentrations in 1985 below the reference concentration of 10 ppm dw.

The overall pattern of sediment lead contamination along the mainland coastal shelf of the Bight has remained relatively unchanged over the decade between 1977 and 1986 (compare Figures 8.2, 8.3, and 8.4). A major difference is that concentrations off Palos Verdes have decreased dramatically from a 1974 60-m mean of about 425 ppm dw to a 1985 mean of about 80 ppm dw (Figure 8.5). Apparently, during the past decade, lead concentrations have also declined near the Orange County outfall (CSDOC, 1987) and at the Newport Bay shipyards (Liu and Schneider, 1988), but may have increased in Marina del Rey and adjacent areas of Santa Monica Bay. They also increased in previously isolated inner Bolsa Bay after tidal gates were lifted in 1978 (Feldmeth, 1980; Christensen et al., 1978).

From a national review of sediment effects data, Long and Morgan (1990) calculated a probable effects range (ER-L to ER-M) for lead of 35 to 110 ppm dw. The lower of these concentrations was exceeded in sediments from Santa Monica Bay, Marina del Rey, Los Angeles-Long Beach harbors, Bolsa Bay, Newport Bay, and San Diego Harbor. The ER-M value was exceeded at Palos Veres, Marina del Rey, Nowport Bay, and San Diego Harbor.

Table 8.1. Mean, median, minimum, and maximum lead concentrations in surface sediment from selected surveys, 1970-85 in ppm dw.

SITE	Year	N	Mean	Median	Minimum	Maximum	Standard Deviation	Source
Rural Coastal Shelf (60 meters only):								
Santa Barbara shelf	1977	11	5.9	5.0	2.7	12	2.9	1
	1985	4	4.1	3.8	2.4	6.6	1.8	2
Port Hueneme to Point Dume	1977	4	5.1	5.1	4.1	6.1	1.2	1
	1980	11	13	10	5.2	29	7.7	3
	1985	2	6.4		4.1	8.6	3.2	2
Newport to Dana Point	1977	3	7.7	7.7	6.3	9.2	1.5	1
	1978	6	10	9.5	7.7	15	2.6	4
	1985	1	9.3					2
Outfall Areas:								
Oxnard shelf	1971[a]	4	16	16	11	20	4.7	9
Santa Monica Bay	1970[a]	24	29	28	2.9	65	14	9
	1977[b]	13	22	16	11	66	16	1
	1978[b]	31	28	24	3.9	138	22	4
	1985[b]	3	86	88	66	105	20	5
Palos Verdes shelf	1970[a]	22	107	92	9.4	350	83	9
	1977[b]	8	178	147	1.8	537	179	1
	1978[b]	8	160	157	27	243	65	4
	1985[b]	10	76	69	18	190	52	5
Orange County shelf	1970[a]	13	29	11	6.1	220	58	9
	1977[b]	11	21	22	5.2	36	7.4	1
	1978[b]	12	12	12	8.8	17	2.8	4
	1985[b]	9	11	11	8.3	19	3.4	7
Point Loma shelf	1970[a]	5	13	11	10	24	6.1	9
	1977[b]	6	9.2	7.4	5.3	19	5.3	1
	1985[b]	8	20	19	16	32	5.0	8
Bays and Harbors:								
Marina del Rey[a]	1977	11	110	94	33	359	89	10
	1978	11	50	38	11	118	33	10
	1984	12	154	139	66	293	84	11
	1985	12	169	143	18	377	104	12
	1987	13	178	121	11	537	149	13
Los Angeles-Long Beach harbors [a]	1973	31	127	102	35	424	88	14
	1978	30	24	17	5	99	21	15
Bolsa Bay - inner	1978	13	12	8	1	26	7.3	20
Bolsa Bay - inner	1980	5	55	52	18	90	31	21
Bolsa Bay - outer	1978	16	62	62	15	107	2.6	20
Bolsa Bay - outer	1980	3	51	42	35	77	22.4	21
Bolsa Bay - flood control	1978	9	26	32	8	45	14	20
Upper Newport Bay	1971	3	18	21	2	30	14	18
Upper Newport Bay[a]	1980	8	24	23	16	39	8.1	16
Lower Newport Bay	1971	7	75	44	18	172	60	18
Newport shipyards	1972	9	1200	994	141	4200	1233	19
Newport shipyards	1980	9	197	190	80	340	87	19
Newport shipyards	1986	6	133	140	90	186	40	19
San Diego Harbor	1974	11	186	231	46	4440	129	18
San Diego Harbor[a]	1984	20	94	74	15	315	76	17
OVERALL					1	4440		

a - all depths; b - 60-m only

Table 8.1 References:

1	Word and Mearns, 1979	8	City of San Diego, original data	15	Soule and Oguri, 1980a
2	Thompson *et al.*, 1987	9	SCCWRP, 1973	16	MBC and SCCWRP, 1980
3	Hershelman *et al.*, 1982	10	Soule and Oguri, 1980b	17	Ladd *et al.*, 1984
4	Hershelman *et al.*, 1981	11	Soule and Oguri, 1985	18	Young *et al.*, 1975
5	Hyperion Treatment Plant, original data	12	Soule and Oguri, 1986	19	Liu and Schneider, 1988
6	CSDLAC, original data	13	Soule and Oguri, 1987	20	Riznyk and Mason, 1979
7	CSDOC, original data	14	Chen and Liu, 1974	21	Feldmeth, 1980

Lead has been a regionwide contaminant of sediments throughout the Southern California Bight since the late 1930s or early 1940s. In dated cores from the Santa Barbara and Santa Monica basins, west of the Los Angeles area, concentrations and apparent fluxes increased threefold between the 1930s and 1970 (Bruland *et al.*, 1974; Chow *et al.*, 1973). In the San Pedro Basin immediately south of the Los Angeles area, concentrations increased fourfold over the same period; and off the eastern end of San Clemente, 100 km south of Los Angeles, concentrations increased about 50 percent. Although no long-term increase appears for lead in the Soledad Basin off southern Baja California, careful inspection of the data in Chow *et al.* (1973) suggests concentrations may have been slightly higher (10 to 20%) after 1900 than before. There is also evidence that concentrations of lead in basin sediments have decreased by as much as half peak values on a regionwide basis since the early 1970s including in the San Pedro Basin (Ng and Patterson, 1982), in the Santa Monica Basin (Finney and Huh, 1989), and in the Santa Barbara Basin (Schmidt and Reimers, 1987). Additional data provided by Ng and Patterson (1982) indicate basin lead concentrations at any point in time were relatively low in the Santa Barbara Basin, intermediate in the Santa Monica Basin, and high in the San Pedro Basin.

Table 8.2 Comparison of median lead concentration in sediments (ppm dw) from the most recent non-NOAA surveys in 18 regions or sites.

Region or Site	Year	Median	Ratio-to-Reference
Newport shipyards	1986	140	14
Marina del Rey	1987	121	12.1
Huntington Harbor [1]	1983-84	92	9.2
Santa Monica Bay	1985	88	8.8
San Diego Harbor	1983	84	8.4
Palos Verdes shelf	1985	69	6.9
Inner Bolsa Bay	1980	52	5.2
Outer Bolsa Bay	1980	42	4.2
Dana Harbor [1]	1983-84	24	2.4
Upper Newport Bay	1980	23	2.3
Tijuana Estuary, south arm [2]	1988	19.6	2.0
Point Loma shelf	1985	19	1.9
Los Angeles-Long Beach harbors	1978	17	1.7
Orange County shelf	1985	11	1.1
Newport to Dana Point	1985	9.3	.9
Port Hueneme to Point Dume	1985	6.4	.6
Tijuana Estuary, north arm [2]	1988	4.0	.4
Santa Barbara Shelf	1985	3.8	.4

1 Data from OCEMA (1986)
2 Data from Gersberg *et al.* (1989); all others from table 8.1.
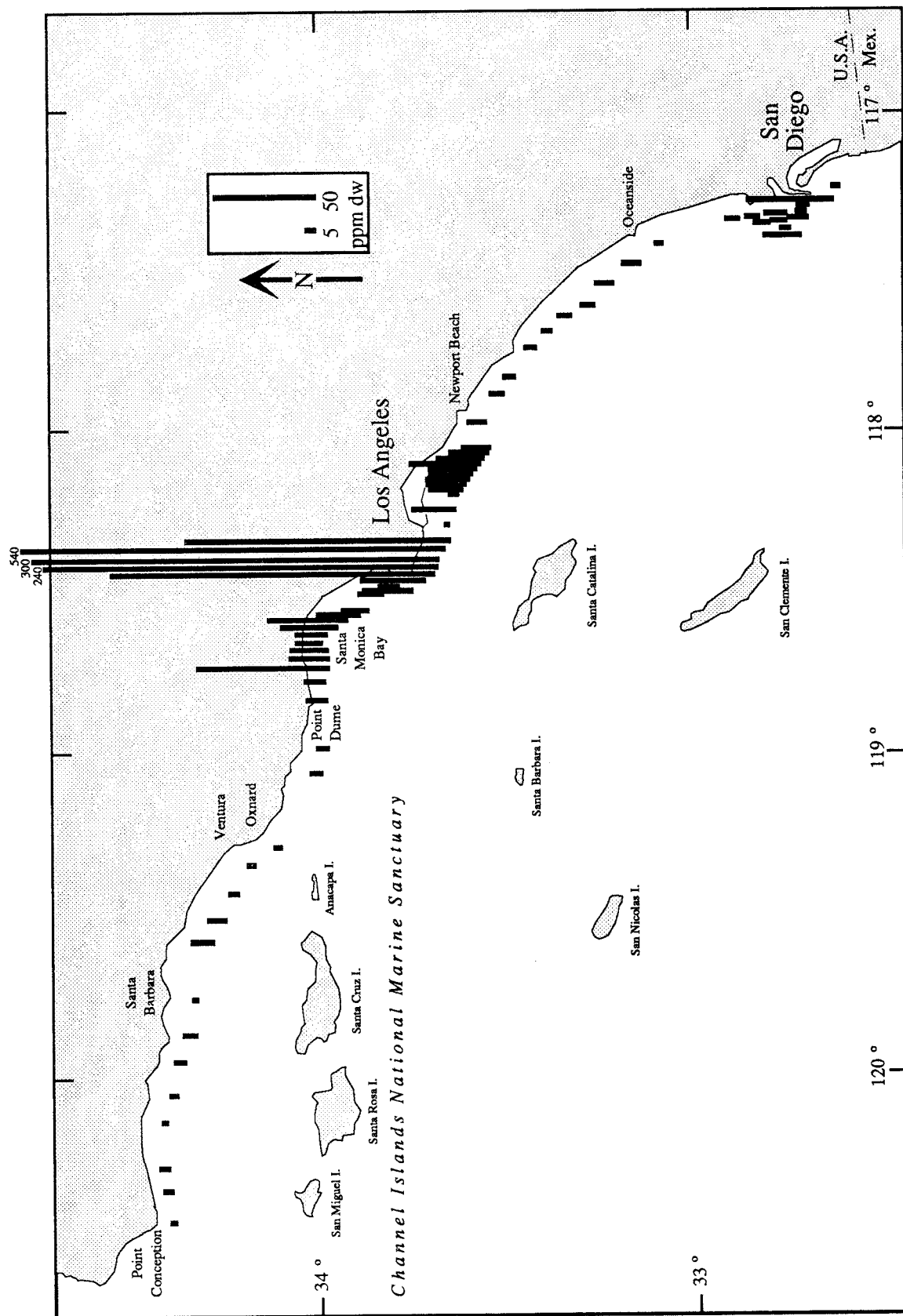
Figure 8.2. Lead concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line, based on data from the 60-Meter Control Survey performed from April through August 1977 (Word and Mearns, 1979).

8-5
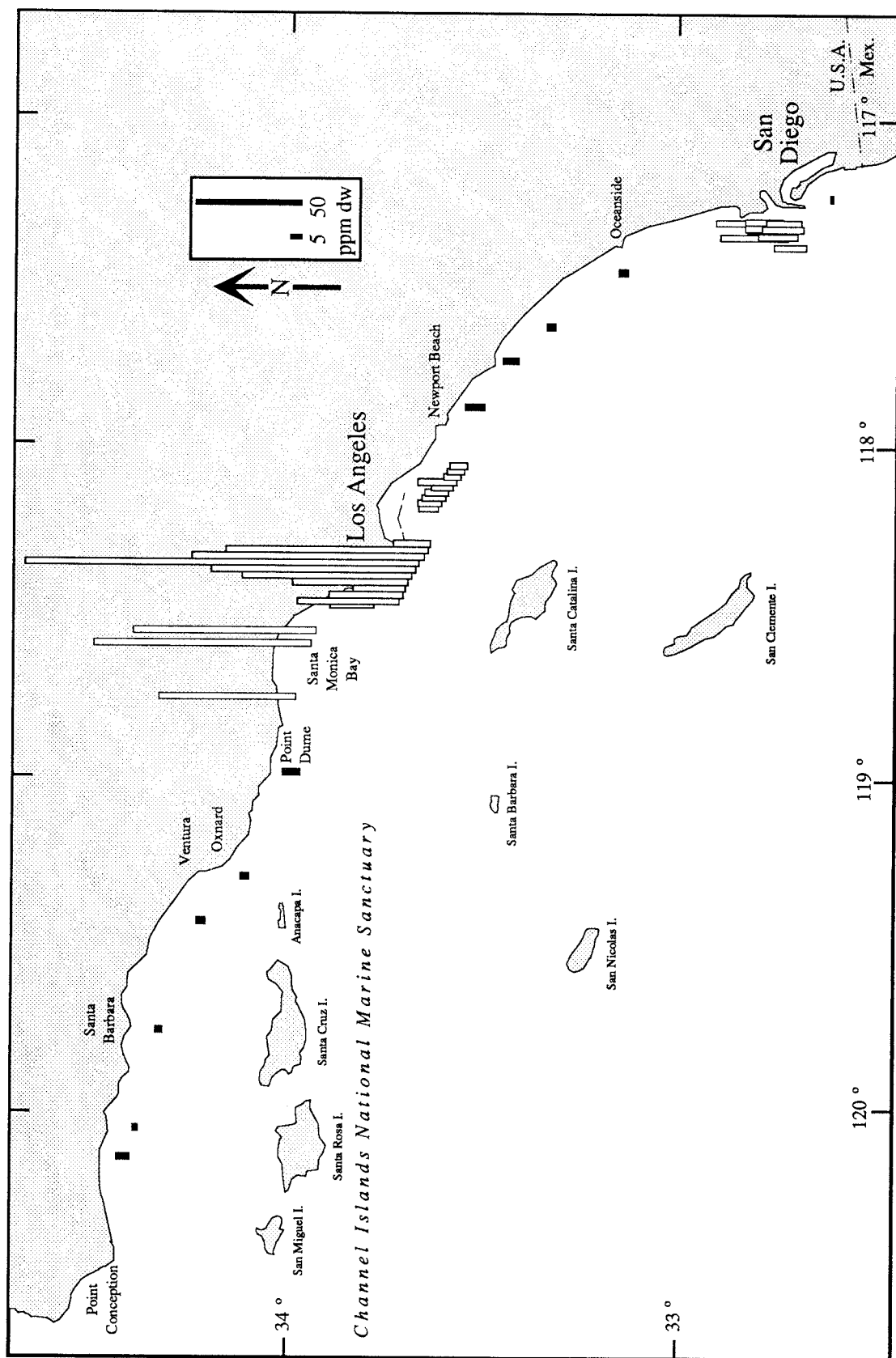
Figure 8.3. Lead concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line for 1985. The black bars are based on data derived from Thompson, et al., 1987. The white bars are based on data obtained from the various sanitation districts (City of Los Angeles, Los Angeles, Orange, and San Diego counties).
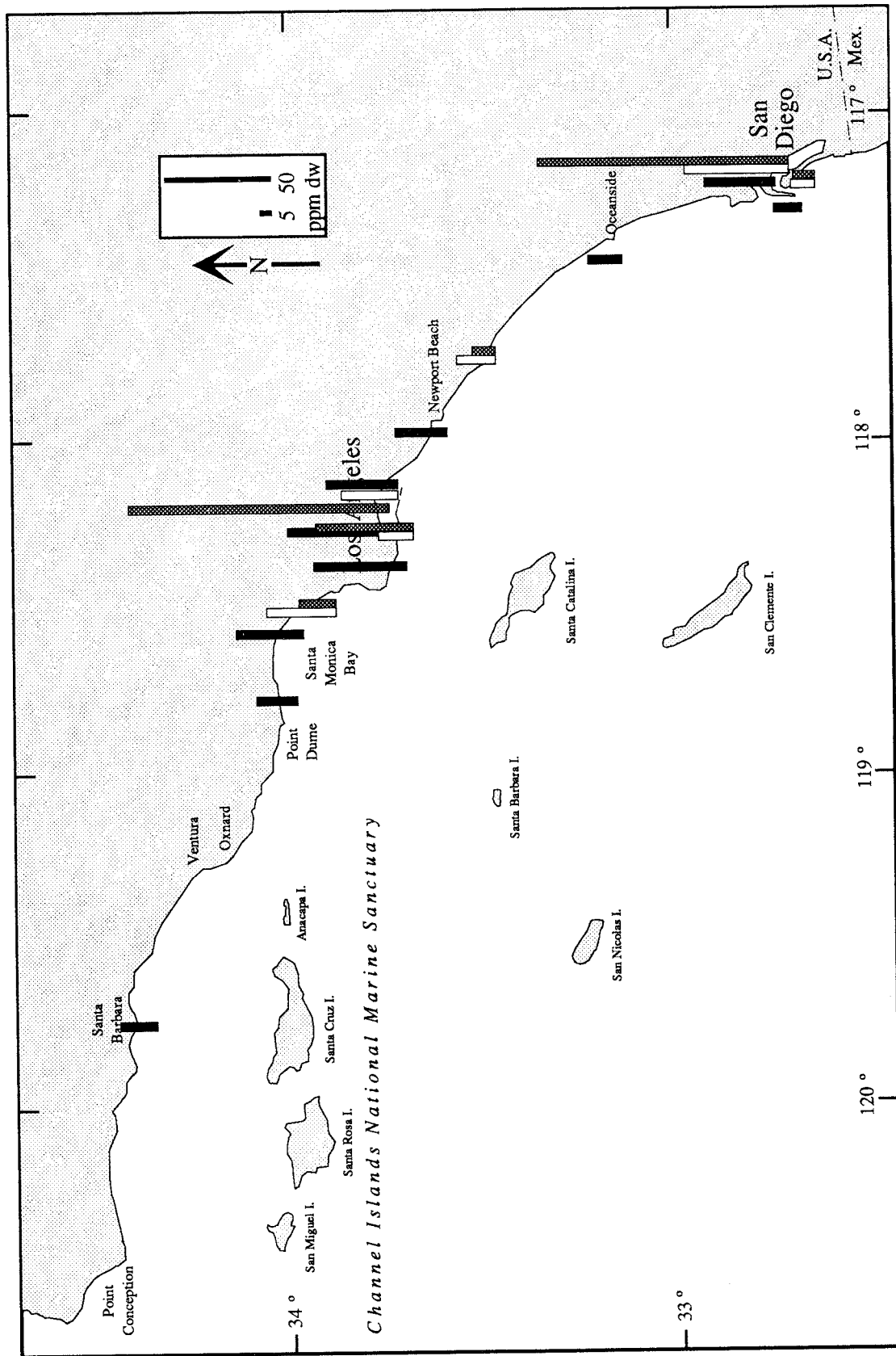
Figure 8.4. Lead concentrations in the surficial sediments of the Southern California Bight Based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 (▌) and 1985 (▌) and Mussel Watch Project for 1986 (▌) (NOAA, 1988 and NOAA, unpublished data).
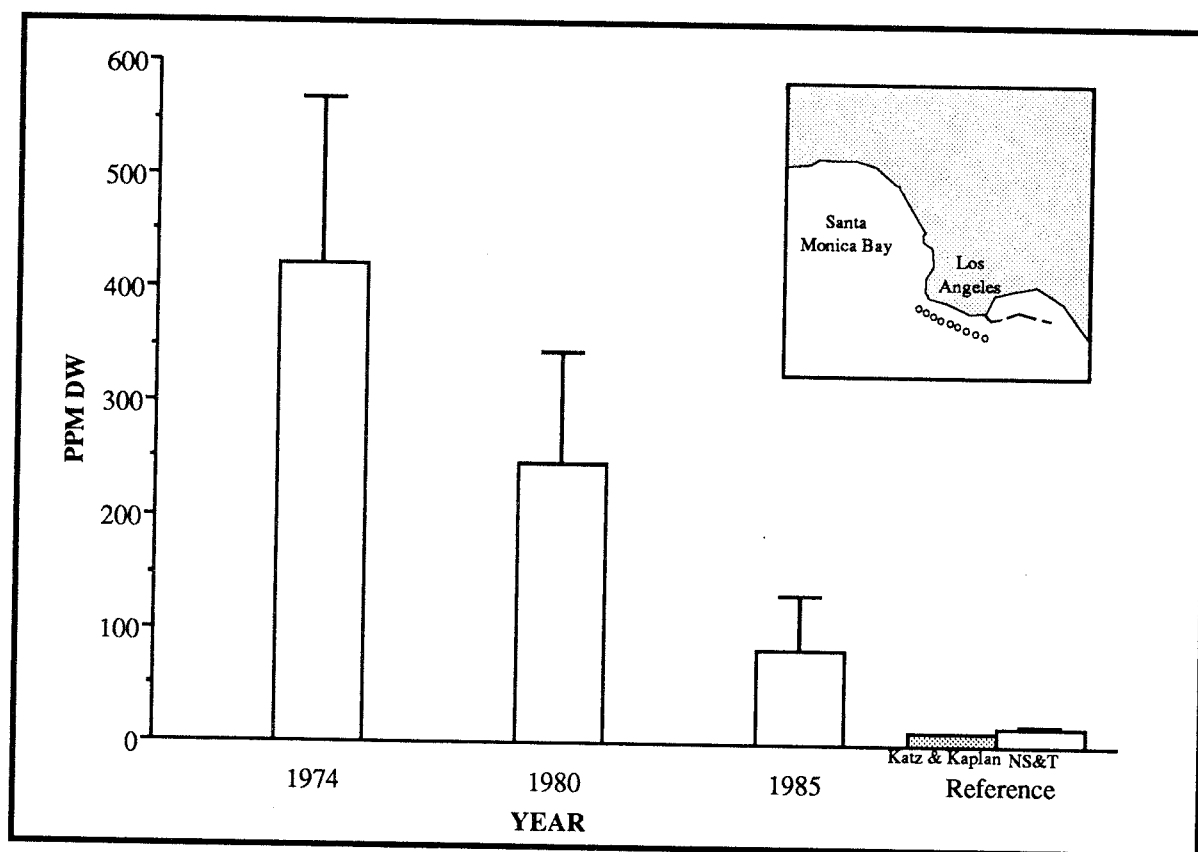
Figure 8.5. Mean lead concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC. The reference values are based on the value reported by Katz and Kaplan (1981) and the mean of four relatively isolated NOAA NS&T Program sites in the Southern California Bight sampled between 1984 and 1986. (NOAA, 1988 and NOAA unpublished data). Inset shows approximate locations of sites sampled by CSDLAC.

LEAD IN MUSSELS

Lead has been analyzed in hundreds of samples of mussels from the Southern California Bight since 1971. There is good regionwide spatial coverage for some years, but evaluation of temporal trends and comparison of various bays and coastal sites is difficult because of intersurvey differences in species and types of tissue analyzed.

A number of studies have compared tissue concentrations of lead between *M. californianus* and *M. edulis*. The data are both limited and inconclusive, and, as a result, no direct cross-species comparisons of lead body burdens are undertaken in the present discussion. Table 8.3 summarizes values for lead when same-site data are available for both mussel species.

8-8

Table 8.3. Comparison of lead body burdens in two mussel species collected at the same sites. Samples are whole soft body tissue, except for Hayes *et al.*, 1985, who analyzed whole soft body less gonads.

Source	Pb in *M. californianus* (ppm dw)	N	Pb in *M. edulis* (ppm dw)	N
Graham, 1972	7.8±1.3	6	7.6±0.3	8
Chow *et al.*, 1976	7.5	3	2.1	3
Goldberg *et al.* 1978	0.77±0.15	*	4.13±1.21	*
	2.24±1.02	*	5.10±1.55	*
Hayes *et al.*, 1985	5.5	45	2.9	45

* not given

Chow *et al.* (1976) reported concentrations of lead in *M. californianus* and *M. edulis* collected in the southern California-northern Mexico region between October 1972 and September 1973. These results are notable because the investigators measured concentrations in whole soft body tissue as well as in discrete organ tissues. They also reported results for wet weight and dry weight concentrations. Chow *et al.* (1976) found that among four soft tissues (muscle, gill, stomach, and gonad) and the two shell halves, gill tissue contained the highest concentrations of lead. This held true for both mussel species. Whole soft body tissue concentrations are compared to those for individual organ tissues in Table 8.4.

Of particular relevance for evaluating the data used for this discussion are the relationships between whole body concentrations and those in digestive gland and gonad tissue. SCCWRP results in 1971 and 1974 were from digestive gland. CMW Program results were for soft body tissues with gonadal tissue excised. EPA and NS&T Mussel Watch results were for whole soft body tissue. While the data of Chow *et al.* (1976) will not permit conversion and direct comparison of concentrations measured in differing tissue matrices, they may enable more general observations to be made. For example, with the exception of *M. californianus* specimens collected at Gaviota State Beach, the results suggest that digestive gland tissue could be expected to yield lower concentrations of lead than whole soft body tissue (Table 8.4) Therefore, the concentrations measured in digestive glands in the 1971 and 1974 SCCWRP studies are probably lower than would have been found in whole body tissue had this been measured. Similarly, because levels of lead in gonad tissue are consistently lower than in whole body tissue, it would appear that excision of gonad tissue, as is called for in CMW protocols, would generally result in higher concentration values than when whole body tissue is analyzed.

Table 8.4. Comparison of whole soft tissue concentrations of lead in mussels to individual tissue concentrations. Values in ppm dw. Chow *et al.*, 1976.

Site	Species	Whole	Muscle	Gill	Digestive Gland	Gonad
Gaviota	*M. californianus*	0.74	0.54	2.55	1.15	0.51
Santa Barbara	*M. edulis*	11.7	2.28	18.8	5.14	2.36
Long Beach	*M. californianus*	17.4	9.31	31.2	7.89	6.43
Scripps Pier	*M. californianus*	7.96	4.75	14.6	2.75	3.28
San Diego	*M. californianus*	8.69	3.26	10.7	3.41	2.16
La Salina (Baja)	*M. californianus*	2.26	1.93	7.09	1.01	1.40
Punta Banda	*M. californianus*	3.01	1.01	3.56	0.89	1.74

Synoptic results obtained in 1971 by Alexander and Young (1976) showed a steady decrease in lead concentrations in digestive gland tissue of *M. californianus* with increasing distance offshore (Figure 8.6). Mean lead concentrations were highest along the mainland coast (18 ppm dw), intermediate along the first line of islands (11 ppm dw; Anacapa, Santa Barbara, and Santa Catalina), and lowest along the outer line of islands (2.7 ppm dw; San Miguel, San Nicolas, and San Clemente). This pattern was strongly indicative of a land-based diffuse source (aerial fallout) rather than the result of specific outfall sources (SCCWRP, 1973). A large-scale dispersion model was developed for predicting first-order, regionwide contamination patterns resulting from three types of sources: (a) outfalls, (b) run-off, and (c) line (atmospheric deposition). The 1971 digestive gland lead concentration had no significant correlation with the outfall sources' prediction, but the line-source predictions accounted significantly for 50 percent of the variation. There was also a slight correlation with the runoff-source predictions (SCCWRP, 1973).

Collection of *M. californianus* at 11 sites between Piedras Blancas in central California and Punta Banda in northern Baja California between October 1972 and September 1973 by Chow *et al.* (1976) reconfirmed and extended the pattern seen by Alexander and Young (1976) along the mainland coast. The range of median concentrations in whole soft tissue were 0.3 to 0.9 ppm dw at four central California sites, 0.8 to 1.1 ppm dw at three sites along the Santa Barbara coast, 3.4 to 7.7 ppm dw at three sites along the San Diego County coast, and 2.4 to 4.1 ppm dw at three sites along the Baja California coast near Ensenada. *M. californianus* was not sampled along the Los Angeles-Orange county coasts or at any of the islands. Lead isotope ratios measured in *M. californianus* and *M. edulis* from five southern California sites were in reasonable agreement with ratios measured in 1969-71 aerosols, confirming leaded gasoline as the origin of the lead (Chow *et al.*, 1976).

Results of the 1986 NS&T Program Mussel Watch Project portray a similar but less distinct regionwide gradient for *M. californianus* 15 years after the Alexander and Young (1976) and Chow *et al.* (1976) surveys (Figure 8.7). Measurements at four Los Angeles-Orange county sites (3.0 ppm dw at Point Dume to 14.5 ppm dw at Anaheim Bay) and at three San Diego area sites (2.4 ppm dw at Point Loma to 5.9 ppm dw at La Jolla) were 2 to 10 times higher than the range of concentration at less urbanized sites at Point Conception, Santa Barbara Point, Santa Cruz Island, and Santa Catalina Island (1.1 to 2.0 ppm dw). In both the 1971 Alexander and Young (1976) survey and the 1986 NS&T survey, the most contaminated *M. californianus* came from the Anaheim Bay-Seal Beach area (Figures 8.6 and 8.7).

Tables 8.5 and 8.6 provide more detailed summaries for lead in *M. californianus* (mainly coastal sites) and *M. edulis* (mainly bay and harbor sites) respectively. Overall southern California coastal averages were about 3.0 ppm dw for *M. californianus* in 1973 (Chow *et al.*, 1976) and again in 1986 (NOAA, 1989). During the 1980 CMW surveys, the overall mean was higher (9.0 ppm dw). The most contaminated *M. californianus* came from Santa Monica Bay in 1980 with a mean of 15.7 ppm dw and a range of 4.1 to 31.0 ppm dw. All other regions produced *M. californianus* with mean concentrations less than half this average. The cleanest areas appeared to be Santa Barbara and the Channel Islands with all concentrations below 2 ppm dw.

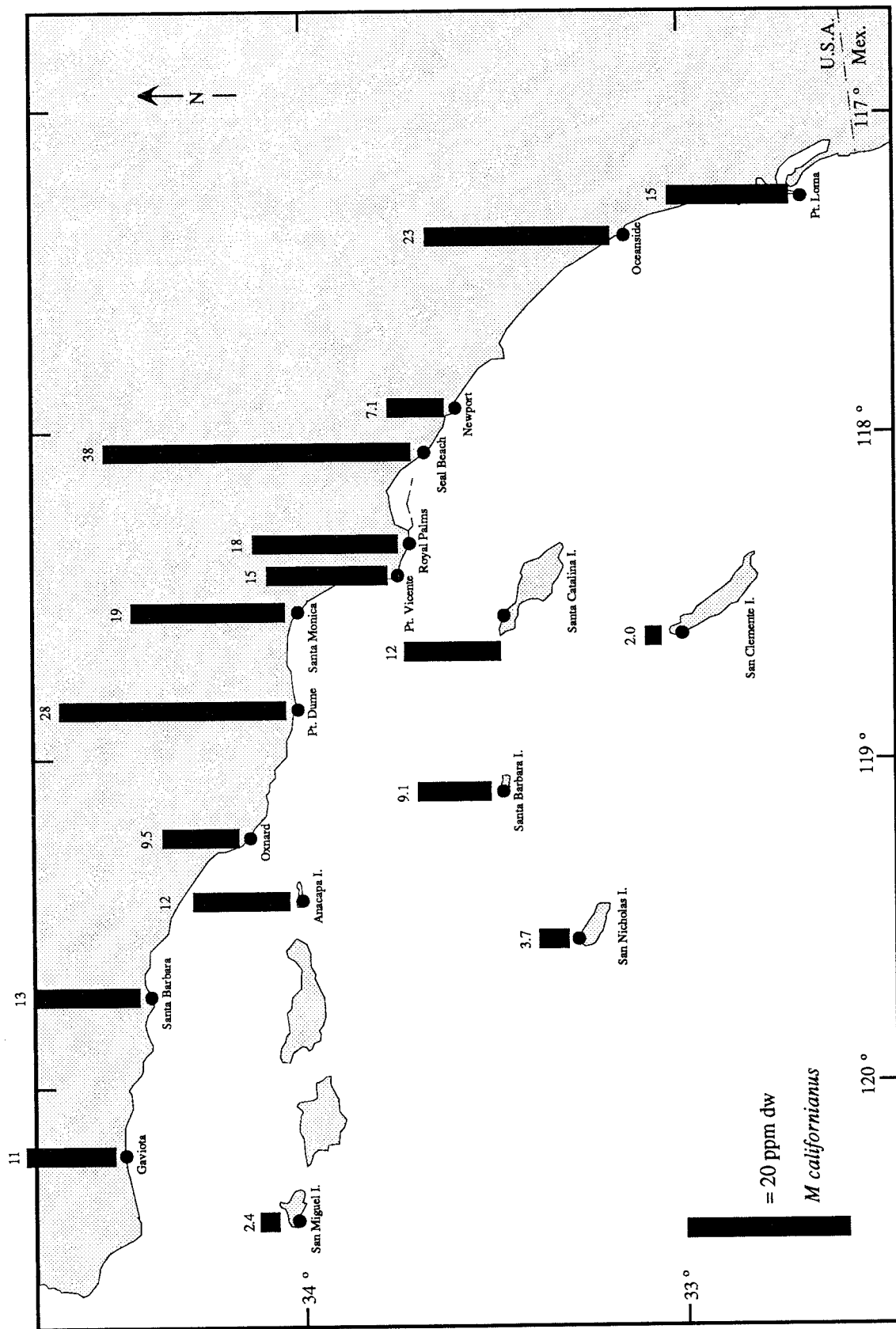Figure 8.6. Concentrations of lead measured in digestive gland tissue of mussels collected in the Southern California Bight in 1971. Values shown are means of six samples, each sample = one individual. Source: Alexander and Young, 1976.
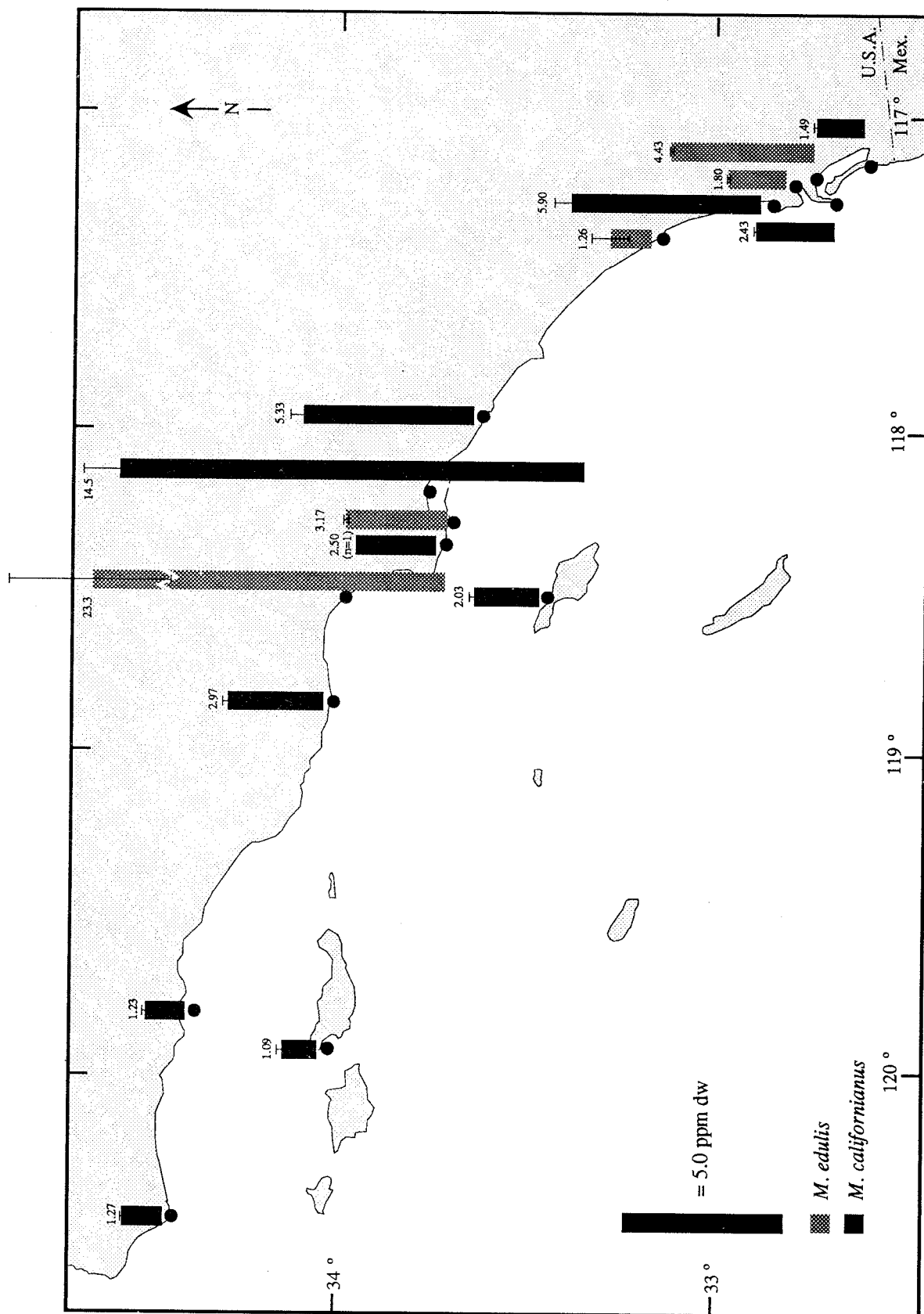
Figure 8.7. Lead in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

Table 8.5. Summary of lead concentrations (ppm dw) in whole soft tissue of *M. californianus* from various sampling areas in the Southern California Bight 1972-86.

Region or Site	Year	N	Mean	Median	Min	Max	SD	Source
All sites	1972-73	8	3.1	2.6	0.7	7.9	2.4	Chow et al. 1976
All sites	1980	30	9.0	5.5	2.0	31.0	8.4	Phillips, 1988
All sites	1986	5	3.3	2.4	1.3	5.9	2.2	NOAA, 1989
Coastal subareas								
Santa Barbara Coast	1973	3	1.0	1.1	0.7	1.3		Chow et al. 1976
Santa Barbara and islands	1986	3	1.5	1.2	1.1	2.0		NOAA, 1989
Santa Monica Bay	1980	10	15.7	14.5	4.1	31.0	10.3	Phillips, 1988
Point Dume	1980	1	4.5					Phillips, 1988
Point Dume	1986	3r	3.0	3.0	2.6	3.3		NOAA, 1989
Santa Catalina Island	1980	5	6.5	2.6	2.0	22.0	8.7	Phillips, 1988
San Clemente to Mission Bay	1973	3	5.3	4.5	3.4	8.0		Chow et al. 1976
Newport to Imperial Beach	1980	13	5.3	4.5	2.0	11.0	2.6	Phillips, 1988
Northern Baja California	1973	2	2.6	2.6	2.3	3.0		Chow et al. 1976

Table 8.6. Summary of lead concentrations (ppm dw) in whole soft tissue of *M. edulis* from various sampling areas in the Southern California Bight 1972-73 and 1980-86.

Region or Site	Year	N	Mean	Median	Min	Max	SD	Source
Santa Barbara Harbor marina	1972-73	6	7.6	4.6	2.5	18.9	6.4	Chow et al., 1976
Channel Islands Harbor	1980	1	2.4					Phillips, 1988
Marina del Rey	1980, 82	2	68	68	49	87		Phillips, 1988
Marina del Rey jetty	1986	3r	23	24	18	28		NOAA, 1989
Los Angeles-Long Beach harbors	1980, 1985	17	13.9	11	4.2	37	10.0	Phillips, 1988
San Pedro breakwater	1986	3r	3.2	3.2	3.0	3.3		NOAA, 1989
Colorado Lagoon	1982, 1985	3	41	37	18	66		Phillips, 1988
Long Beach Harbor marina	1973	5	17	20	8.1	25	8.1	Chow et al., 1976
Anaheim Bay fuel dock	1973	5	33	32	24	36	6.5	Phillips, 1988
Anaheim Bay sites	1980, 1982	2	19	19	8.4	29		Phillips, 1988
Newport Bay	1980-1985	4	6.6	6.2	4.2	9.7	2.5	Phillips, 1988
Newport pier	1980	1	2.9					Phillips, 1988
Oceanside Harbor marina	1973	5	6.5	5.7	4.9	10	2.1	Chow et al., 1976
Oceanside Harbor	1985	1	13					Phillips, 1988
Mission Bay	1980, 1982	5	2.7	2.2	1.8	5.3	1.5	Phillips, 1988
Point Loma	1983	1	1.7					Phillips, 1988
San Diego Harbor marinas	1973	9	6.4	4.9	1.5	12.9	4.3	Chow et al., 1976
San Diego Harbor	1980, 1982	4	4.2	5.3	1.2	6.6	2.3	Phillips, 1988
San Diego Harbor Island	1986	3r	4.4	4.5	4.3	4.5		NOAA, 1989
Ensenada Harbor marina	1973	4	3.8	4.1	1.2	5.7	1.9	Chow et al., 1976

There was an unusual distribution of lead concentrations in Santa Monica Bay *M. californianus* sampled in the CMW Program in 1980. Figure 8.8 shows an apparent pattern of elevated tissue concentrations of lead in the lower half of Santa Monica Bay from Marina del Rey south. Applying the nonparametric statistic, the Mann-Whitney test (Snedecor and Cochran, 1980), lead concentrations north of Marina del Rey in Santa Monica Bay were determined to be significantly lower from those south of Marina del Rey, at the p = 0.05 level of significance.

The general direction of nearshore surface water circulation in Santa Monica Bay has been described as southeasterly (Emery, 1960). If, as has been indicated by results from both the NS&T Mussel Watch Project and the CMW Program, there is a source for elevated levels of lead in Marina del Rey or in run-off from Ballona Creek, the distribution of *M. californianus* tissue lead concentrations may reflect this interaction between input sources and physical mechanisms of dispersion.

Regional differences of lead contamination have been even more striking in *M. edulis* than in *M. californianus*. Higher lead concentrations have been found in *M. edulis* from bays, lagoons, and harbors in the Los Angeles area than in comparable areas of Santa Barbara, Ventura, Orange, and San Diego counties. For example, mean lead concentrations in five Los Angeles area harbors, marinas, and lagoons (Marina del Rey to Anaheim Bay) were mostly above 10 ppm dw (range 3.2 to 68 ppm dw; Table 8.6). Whereas, all other harbors sampled were always below 10 ppm dw (range 3.8 ppm dw for Ensenada Harbor in 1973 to 7.6 ppm dw in Santa Barbara Harbor marina, also 1973; Table 8.6). The highest concentration was 87 ppm dw in *M. edulis* from the north docks of Marina del Rey sampled in the 1980 CMW survey.

For *M. edulis* sampled in the NS&T Mussel Watch Project, the average tissue lead concentration at Marina del Rey exceeded that at the Oceanside beach jetty by a factor of nearly 18 (23.3 ppm dw versus 1.3 ppm). The elevated levels found at Marina del Rey may reflect inputs from boating activities (fuel residues and antifouling paints). It could also be indicative of proximity to Los Angeles and its high-density automobile traffic (with inputs originating from such mechanisms as aerial deposition and storm water run-off at Ballona Creek).

These relatively high levels of lead found by the NS&T Mussel Watch Project in the Marina del Rey area are corroborated by results from CMW Program sampling. In 1980, *M. edulis* sampled there had a concentration of 87 ppm dw, over 20 ppm greater than the next highest concentration measured from 1977 through 1985. Stephenson *et al.* (1980a) suggested antifouling vessel paints and storm water run-off from nearby Ballona Creek as potential sources for lead in mussels in Marina del Rey.

Figures 8.9 and 8.10 illustrate results for lead in *M. edulis* from the 1974 SCCWRP harbors study and 1980 CMW Program, respectively. Although these include a limited number of sites within San Diego Harbor, both studies show an apparent spatial trend of increasing concentrations into the harbor. This is not unexpected, given the known association of lead with industrial activities and fuel products.

Concentrations of lead in mussels from southern California have generally exceeded the overall national average lead levels found by NOAA's NS&T Program. Between 1984 and 1989 the overall mean lead level in *M. californianus* was 2224 ppm dw (median 1.267 ppm dw). For *M. edulis* the overall mean was higher, 3774 ppm dw (median 2217 ppm dw). The range of site means was greatest for *M. edulis* (below detection limits to 37.667 ppm dw).

Beginning in 1975, new cars were built with catalytic converters requiring the use of unleaded gasoline. Largely as a result of declining emissions of lead from gasoline combustion, U.S. EPA monitoring efforts showed a 64 percent decrease in ambient air levels of lead between 1975 and 1982 (U.S. EPA, 1984).

A declining trend of lead concentrations in mussels in the Southern California Bight apparently reflects the increasing use of unleaded gasoline as a fuel. The most complete long-term information is available from two sites monitored for the CMW Project, located at Royal Palms State Park on the Palos Verdes Peninsula and at Oceanside (1977-86).

At Oceanside, lead concentrations decreased significantly (p ≤ .01) from about 4 in 1977 to about 1 ppm dw during 1983-86. Concentrations at Royal Palms also decreased significantly from about 14 to 18 ppm dw in 1977 to about 6 to 9 ppm dw during the period 1982-86 (Figure 8.11). In both cases, however, most of the decline occurred between 1977 and 1980-81. Concentrations at Oceanside may have approached background, but those in mussels from Royal Palms remained 6 to 9 times higher than at Oceanside during the mid-1980s.
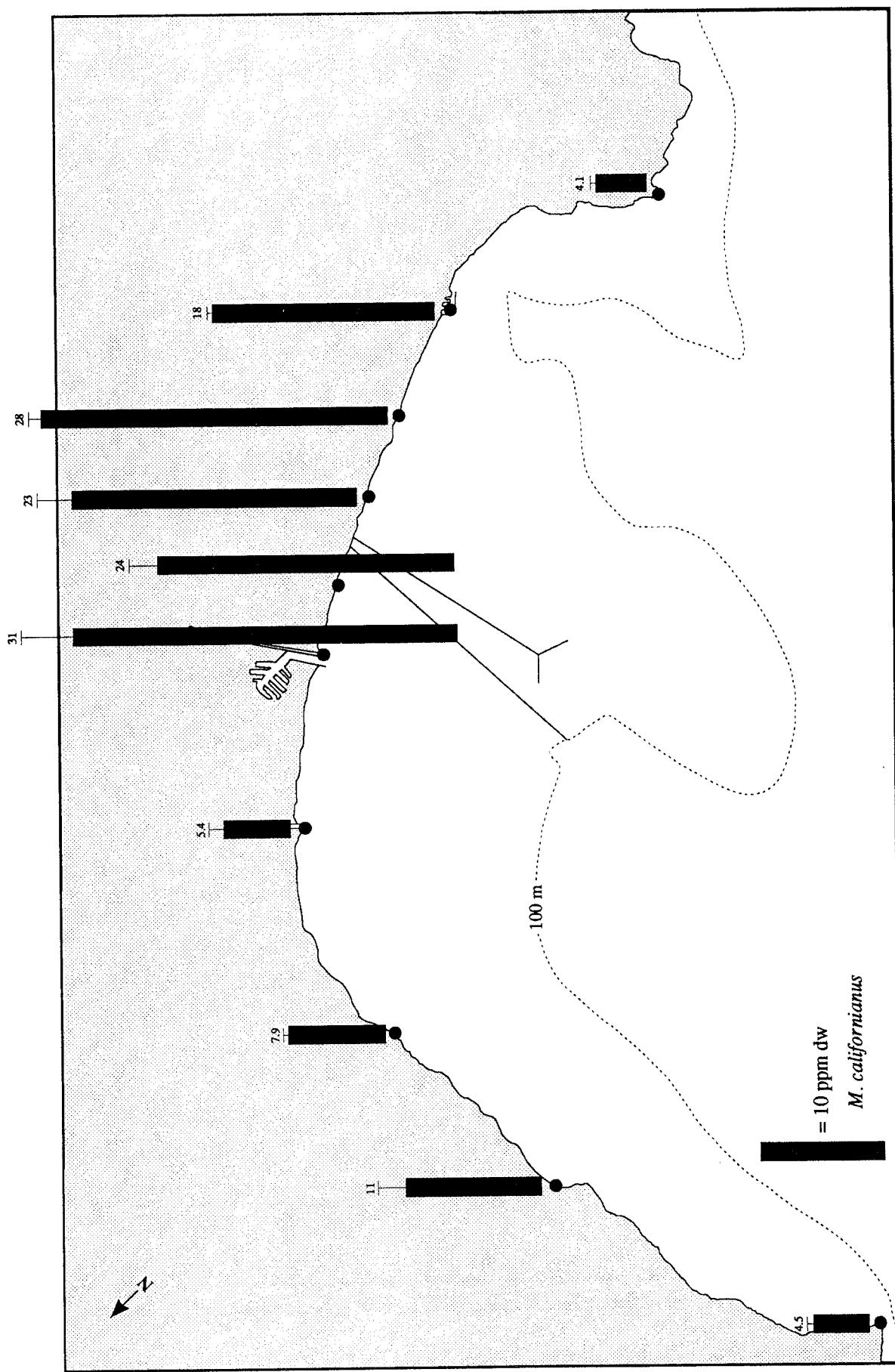
Figure 8.8. Lead in soft body tissue, less gonads, of whole mussels sampled in Santa Monica Bay in 1980. Source: Phillips, 1988.
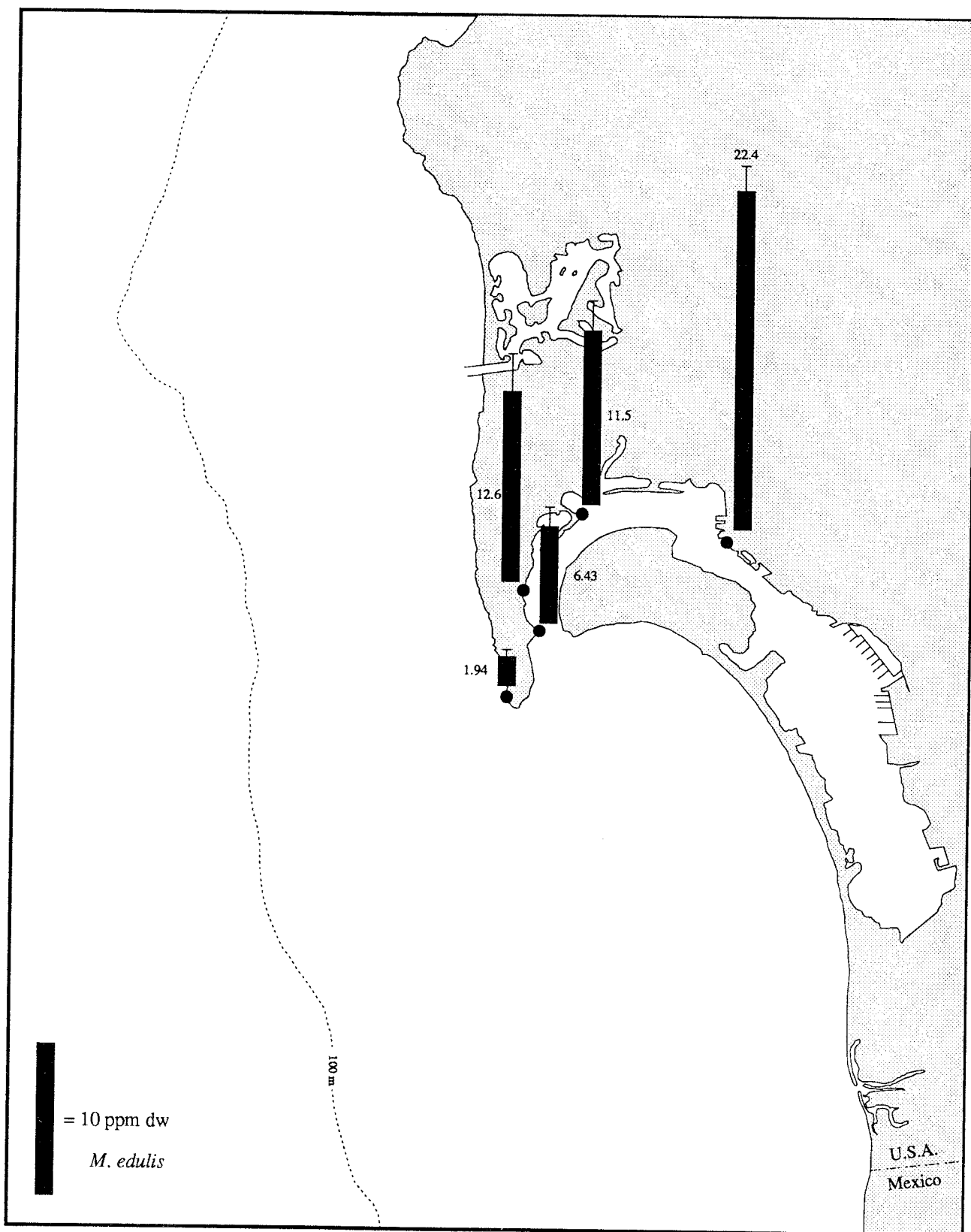
Figure 8.9. Concentrations of lead measured in digestive gland of mussels sampled in San Diego Bay in 1974. Source: Young et al. (1979).
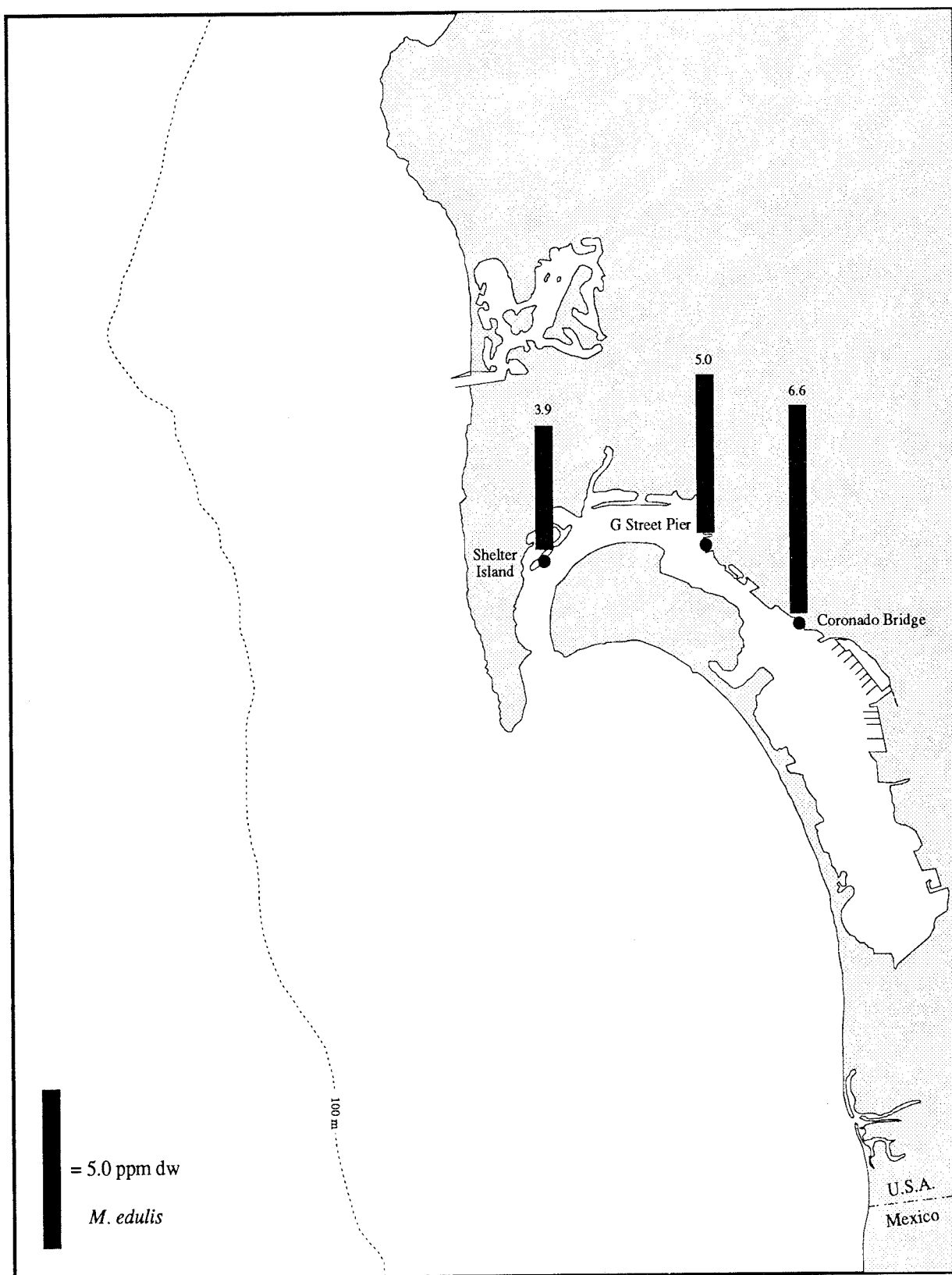
Figure 8.10. Concentrations of lead measured in whole soft body tissue (less gonads) of mussels sampled in San Diego Bay in May 1980. Source: Phillips, 1988.
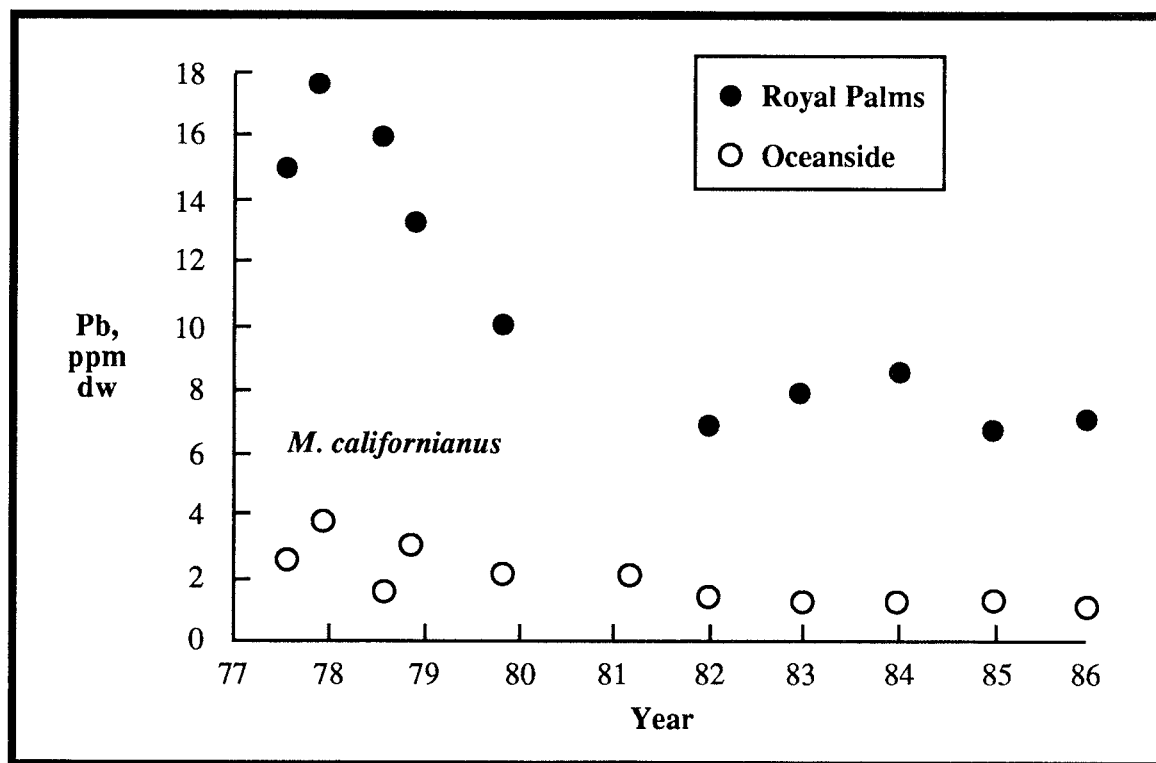
Figure 8.11. Time series of lead concentrations measured in mussels collected at Royal Palms and Oceanside between 1977 and 1985. Source: Phillips, 1988.

Data from an intermediate site, the San Pedro breakwater, modify the trend described above. The EPA Mussel Watch Program encountered an apparent trend of increasing lead concentrations (9 to 18 ppm dw) between 1976 and 1978 (Figure 8.12). When the site was next visited in 1982, the CMW obtained a concentration of about 6.7 ppm dw. When occupied by the NOAA NS&T Mussel Watch Program between 1986 and 1988, the concentration was about 3 ppm dw (NOAA, 1989). Additional evidence also suggests maximum lead contamination along the coastal shelf occurred during the mid-1970s with levels increasing before and falling after 1977-78. The ratio of mean lead concentrations in digestive glands of *M. californianus* from five coastal sites (15.8 ppm dw) to lead in the same species from three island sites (8.8 ppm dw) in 1971 (Alexander *et al.*, 1976) was 1.8. During the 1977 CMW survey, the ratio of concentration from five comparable coastal sites (12.3 ppm dw) and five island sites (3.1 ppm dw) was twice as large (3.9). However, by the 1986 NOAA NS&T Mussel Watch this coastal-to-island ratio decreased to 2.2 (coastal mean, 3.4 ppm dw; island mean 1.6 ppm dw) indicating a lessening of the regional gradient. Together, all the data reviewed above suggest that lead concentration in mussels in the San Pedro Bay area increased to a peak in 1977 or 1978, then declined rapidly through 1981-82, then either declined slowly or not at all through 1986 (but were still elevated). This trend is not inconsistent with patterns of lead usage and emissions documented by the EPA. Even though the use of catalytic converters and unleaded fuel began in 1975, ambient lead levels, lead consumed in gasoline, and average human blood levels of lead continued to increase until 1977 or 1978 (EPA, 1984). These data appear to reflect increasing lead concentrations until 1976-78 and decreasing lead concentrations since the late 1970s. The NOAA NS&T Mussel Watch Program documented no significant changes in lead concentrations in mussels from sites in southern California between 1986 and 1988 (NOAA, 1989).
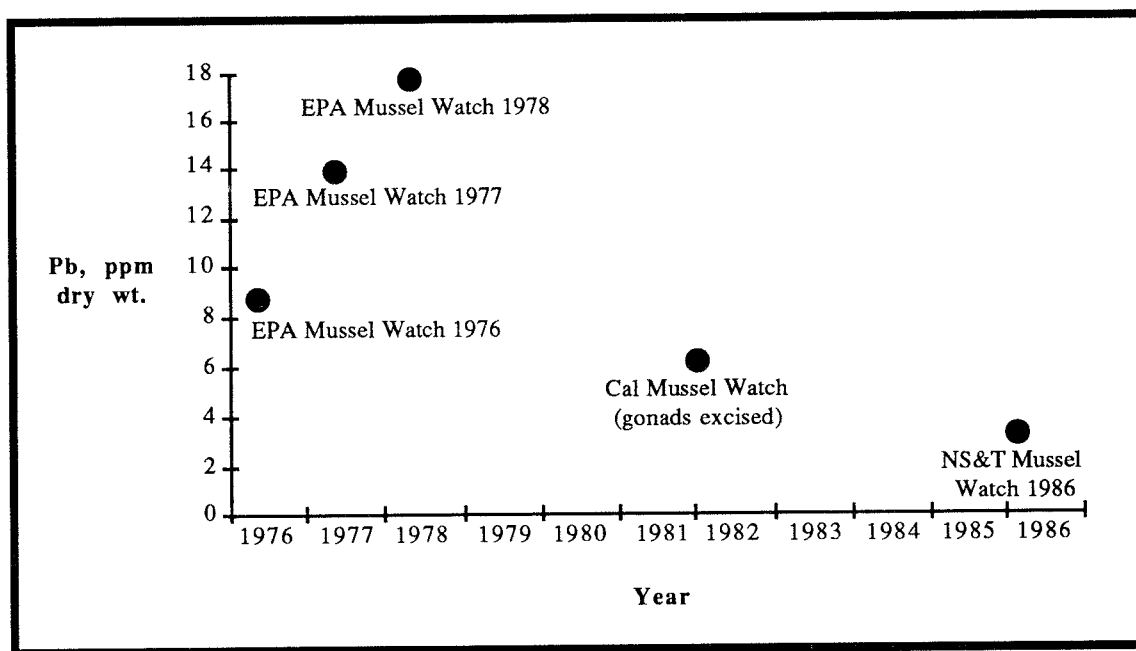
Figure 8.12. Plot of lead tissue concentration results in San Pedro Harbor breakwater M. edulis from three surveys, by year. Phillips, 1988; NOAA, 1989.

In summary, synoptic surveys of mussel tissues or whole soft parts of mussels demonstrate that there has been a large-scale gradient of lead contamination in the Bight increasing toward the Los Angeles area in general, and Los Angeles area bays and harbors in particular. Although the impression is that these bays and harbors may have been major sources, this pattern is not inconsistent with a gradient induced by aerial fallout and or run-off. Further reduction and analysis of these data, coupled with air circulation and atmospheric transport data is needed to confirm the hypothesis that atmospheric inputs have dominated the spatial distribution of lead in intertidal mussels. In this connection, it is interesting that of three simple source-transport models tested ("outfall," "run-off," and "line" source), the latter (line source) best predicted the spatial pattern of the 1971 SCCWRP Mussel Watch lead data (SCCWRP, 1973).

Although lead contamination of mussels along the mainland urban coast near Los Angeles is lower now than during the mid 1970s, concentrations still remain about twice the levels observed at offshore island stations. Apparently, there remain sufficient lead inputs to maintain elevated levels in mussels from this region.

LEAD IN FISH AND OTHER SPECIES

Although there are hundreds of analyses of lead in tissues of fish and macroinvertebrates from the Southern California Bight, most of the data are probably unreliable because dissections and extractions performed in other than ultraclean laboratories result in lead contamination of samples from air, from lead adhering to surfaces, and contaminated reagents (Burnett and Patterson, 1980b; Burnett et al., 1980; and Schaule and Patterson, 1980). However, results of analysis of samples processed in ultraclean laboratories and analyses of tissues containing higher concentrations of lead (such as observed in sediments and whole bivalves) are probably reliable. Fish liver tissue may contain enough lead to ensure reliable results.

Using ultraclean collecting methods and laboratory procedures, Burnett (1980) measured lead in various tissues of marine plants and animals from several widely separated sites in the Southern California Bight. Concentrations in kelp blades were comparable to or higher than those in a herbivorous snail (Haliotis), abalone, and rock scallops. Invertebrate muscle concentrations ranged from 0.004 ppm ww in a rock scallop from Cortez Bank to 0.049 ppm ww in one of several kelp snails (Norrisia norrisii) from the north side of San Clemente Island. With the

exception of the rock scallops, there was little evidence that muscle tissues of Palos Verdes invertebrates contained more lead than those from offshore sites. The data are inadequate for confirmatory statistical testing. In contrast to the invertebrates, an albacore tuna (*Thunnus alalunga*) collected from offshore contained 0.0003 ppm ww of lead in skeletal muscle tissue (Patterson and Settle, 1977). These and other data led Burnett (1980) and Burnett and Patterson (1980b) to conclude that lead does not undergo biomagnification in marine organisms but, instead, undergoes what they term "biodepletion." Further, analysis of kelp or invertebrates lead Burnett and Patterson (1980a) to conclude that the exposed and external parts of animals are more contaminated near lead sources (near Los Angeles) than in remote areas (Cortez Bank). They also concluded that surveys of whole animals (such as done in mussel watch programs) mainly quantify lead that is superficially attached to the animals and not lead that has been taken up biologically in the internal mass (about 1% of measured lead). Even so, that lead which was recorded from muscle and other tissue was considered excess lead and indicative of regional contamination, albeit at extremely low concentrations.

Concentrations of lead in liver of fish from the 1984 NOAA NS&T Benthic Surveillance Program ranged from about 0.01 ppm ww in hornyhead turbot from San Pedro Canyon and white croaker from Dana Point to 0.10 in hornyhead turbot from Dana Point (Figure 8.12). Among the three species collected at six sites by the NS&T Program, there is no consistent pattern indicative of higher concentrations in urban and industrial areas (such as Santa Monica Bay, San Pedro Canyon, Seal Beach, or San Diego Harbor) than in more remote or offshore "reference" areas such as Dana Point or San Diego Bay (outside the harbor; Figure 8.13).

There are no seafood criteria for lead in the United States. Nauen (1983) cites ten international criteria that range from 1 to 6 ppm ww (median, 2 ppm ww). The lowest is nearly 10 times higher than the highest mean value in NS&T Program fish livers and more than 100 times higher than in tissues of marine animals analyzed by Burnett (1980) in an ultraclean laboratory. However, mussels with dry weight concentrations more than 10 ppm, may yield wet weight concentrations more than 1 ppm. Historically, such values have been obtained from Los Angeles area *M. edulis*.

SUMMARY AND CONCLUSIONS

Atmospheric sources have dominated lead inputs to the Southern California Bight; sewage and run-off have been of secondary importance. Sewage inputs have clearly decreased, while aerial and run-off inputs may have decreased.

Lead contamination of coastal sediments and mussels reflect a regionwide decreasing lead gradient from the Los Angeles basin. Local lead gradients in sediments also occurred near shipyards and concentrations were generally higher in marinas and harbors. Mussels were most contaminated in harbors near the Los Angeles basin, with gradients extending into Santa Monica Bay and toward San Diego and Baja California. Mussels from the Santa Barbara area had particularly low concentrations. Marina del Rey, Los Angeles Harbor, and San Diego Harbor have been particularly contaminated. Although concentrations of lead in mussels along the mainland coast of Los Angeles have decreased, they are not yet as low as those found at offshore islands. Due to uncertainties about the quality of lead measurements in animal tissues, we elected not to include analyses of lead in fish from various local and regional monitoring surveys. This does not mean all those data are incorrect, only that additional effort is needed to determine which data were produced under acceptable conditions.

It is possible that current levels of lead in auto emissions are sufficient to maintain elevated levels in sediment and mussels. A review of current non-point source inputs would help resolve this question. Evidence from ultraclean laboratory dissection indicates that only a small fraction of the existing lead was biologically incorporated into tissues of bivalves. The balance of lead measured in mussels is from adsorbed contamination but, nonetheless, may be of concern from a public health standpoint. Further, the analyses support the theory that lead undergoes biodepletion in marine food webs of the Bight.
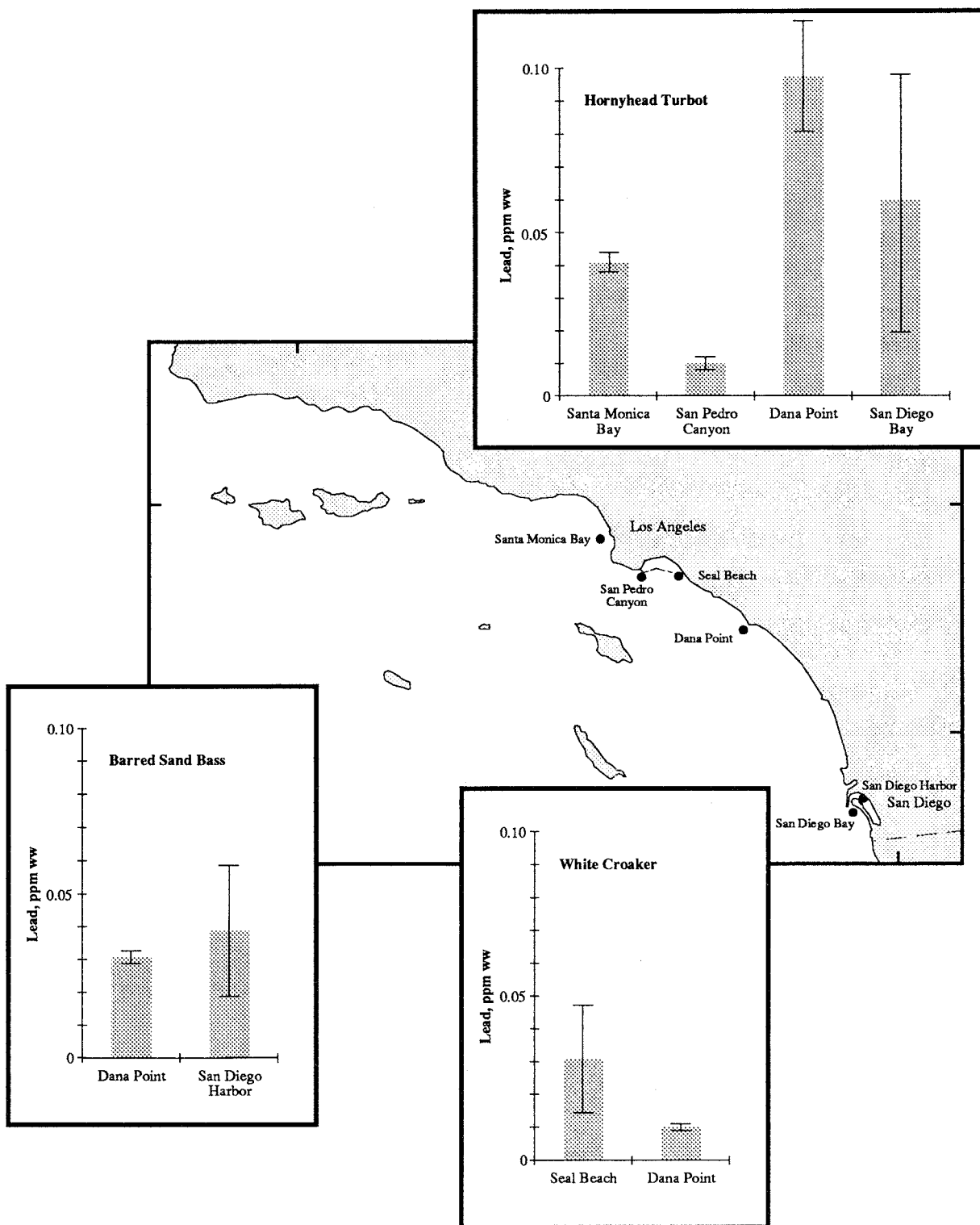
Figure 8.13. Concentrations of lead measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

INFORMATION NEEDS

Although concentrations of lead in sediments and mussels have decreased considerably in recent years, levels remain high along much of the Los Angeles coast. It is possible that current fluxes from auto emissions are still high. Lead monitoring in mussels and sediments at contaminated and apparent reference sites should be continued. Inputs should be better defined and placed in a context of global cycling. Whether significant or not, public health risks of consuming lead contaminated shellfish needs to be estimated and put into a useful perspective. In addition, invertebrate seafood organisms from Palos Verdes previously sampled for lead in 1975-76 should be resampled to confirm that concentrations have declined in concert with decreasing inputs. Measurements of lead in internal organs of fish, shellfish, and wildlife from past and on-going monitoring programs need to be reviewed for adherence to clean field and laboratory protocols. Data sets that pass quality assurance review need to be identified. Lead should probably be dropped as a tissue monitoring analyte from programs that fail to meet clean field collection and laboratory methods.

CHAPTER 9

MERCURY

Mercury is a common trace element with no known biological function. Most of the anthropogenic mercury discharged into the environment is traceable to chlor-alkali plants employing the mercury-cell process. These plants produce chlorine and caustic soda by using saturated brine and mercury streams as a cathode in an electrolytic reaction (Beszedits, 1979). Mercury is also used in fungicides, slime control agents, plastics and electrical equipment, dental preparations, as a chemical catalyst, and in mining and smelting operations (Eisler, 1987; Laws, 1981). In addition, mercury mining has been an important source of contamination in California.

The chemistry of mercury is complex. Some generalizations, however, may be made. While most organic mercury compounds are highly toxic, methylated mercury is notably so (Carty and Malone, 1979). The toxic mechanism of methylmercury derives from its high stability and its ability to penetrate biological membranes (Beijer and Jernelov, 1979). Methylation of mercury may occur both through biotic and abiotic mechanisms, with potentially serious environmental consequences. The presence of sulfides suppresses methylmercury production because sulfide binds mercury to an insoluble form. Organic mercury can be concentrated in successively higher trophic levels. It is a mutagen, teratogen, and carcinogen and is known to cause embryocidal, cytochemical, and histopathological effects. Inorganic forms of mercury are thought to be less toxic.

Environmental mercury fluxes are not well understood. On a global scale, the largest input of mercury may be from natural sources, such as volatilization or sublimation from crustal rock (Laws, 1981). In addition, there is no convincing evidence that fluxes to the ocean have changed significantly in recent years. However, these are global scale observations. There is no question that local anthropogenic inputs of mercury can and have had devastating effects on the environment in specific areas. The best known example is that of Minamata, Japan, where industrial release of methylmercury contaminated the local marine environment. Edible fish and shellfish accumulated levels of methylmercury that subsequently were responsible for hundreds of cases of acute and chronic mercury poisoning. A less familiar, but even larger, outbreak of methylmercury poisoning occurred in Iraq in 1971-72. More than 6000 hospitalizations and nearly 500 deaths resulted from eating bread prepared with seed wheat treated with a mercury fungicide, (National Research Council, 1978).

Available information on mercury in the open ocean shows a large degree of variability in concentrations, both geographically and with depth. Williams et al. (1974) speculated that high concentrations encountered in some regions of the world oceans may be due to volcanism. However, Fitzgerald (1979) observed that the dearth of reliable data on oceanic mercury distributions effectively prevents the development of distributional baselines or the relation of concentrations to biological or physical cycles.

Submerged and surface geothermal springs and coal-fired power plants may be important local, if not regional, natural sources of mercury in this coastal area. Although mercury concentrations in Punta Banda (Baja California) submarine hot spring water was low, mercury concretions on nearby rocks were as high as 7000 ppm dw and contained small red pigmentations attributed to cinnabar (Vidal et al., 1978). On the eastern slope of the mountains of northern Baja California (due east of Ensenada and Punta Banda), fish taken from the Rio Hardy below the Cerro Prieto geothermal field had levels of mercury 3 to 5 times higher than in fish taken upstream or away from the fields (Gutiérrez-Galindo et al., 1988). This system discharges about 0.005 mt per year of mercury into the Rio Hardy, but an order of magnitude more (0.059 mt per year) is discharged into the atmosphere (Robertson et al., 1977).

SCCWRP (1973) estimated, that in 1971 the dominant source of anthropogenic mercury to the Bight was direct rainfall, accounting for 47 percent (8 mt) of the total non-advective input of 17 mt. Vessel coatings and sewage were the second and third sources (4 and 3 mt per year, respectively) and ocean dumping the fourth (1.5 mt per year). Run-off was a minor input (0.1 mt or 0.6%). Although there have been more recent studies of pollutant inputs (Schafer and Gossett, 1988), none have included mercury. The present status of inputs is uncertain except for those from sewage.

Recent data from SCCWRP indicate that inputs of mercury by way of the discharges of municipal treatment plants in the Southern California Bight have declined since the 1970s (Figure 9.1). Mean yearly inputs declined from 2.6 mt in 1974-76 to 1.1 mt 1983-85, and less than 1 mt in 1987 (SCCWRP, 1988). Many measurements of mercury in sewage are now below prevailing detection limits. As a consequence, it is not known how low actual inputs are.
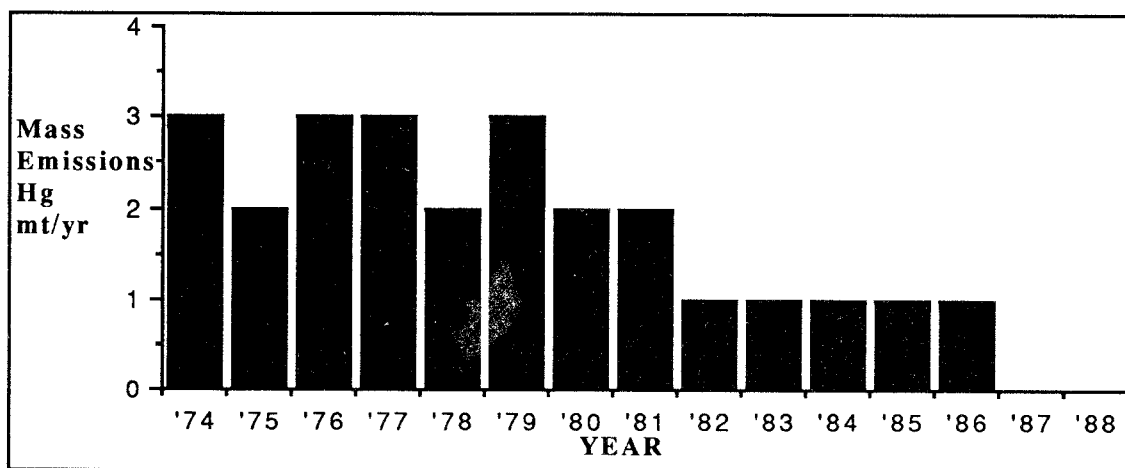
Figure 9.1   Combined annual mass emissions of mercury for seven southern California wastewater dischargers, 1974-86.   Emissions for 1987 and 1988 were less than 1 mt per year.   Source: SCCWRP, 1989.

MERCURY IN SEDIMENTS

There has been no single large-scale survey of mercury in sediments of the Southern California Bight. It was not included as an analyte in the 1977 SCCWRP 60-m survey (Word and Mearns, 1979) or the 1985 SCCWRP Reference Survey (Thompson et al., 1987). The most comprehensive surveys that included mercury were the Galloway (1972a and b) 1970-71 and SCCWRP 1971-72 surveys around five major discharge sites near Oxnard, in Santa Monica Bay and off the coastal shelves of Palos Verdes, northern Orange County and Point Loma (and with reference sites at Santa Catalina Island). The data from these surveys were reported by Eganhouse et al., 1976 (Figure 9.2).

Mercury has been included as an analyte in many localized surveys in harbors and around wastewater discharges. From these, we isolated single-survey data sets for Bolsa Bay (Feldmeth, 1980), Upper and Lower Newport Bay (MBC and SCCWRP, 1980; Young et al., 1975; Liu and Schneider, 1988), Los Angeles-Long Beach harbors (Chen and Lu, 1974; Soule and Oguri, 1980a), San Diego Harbor (Young et al., 1975; Ladd et al., 1984), and Marina del Rey (Soule and Oguri, 1987).

As summarized in Table 9.1, sediment total mercury concentrations from these selected surveys ranged over 15,000-fold, from 0.01 ppm dw at a site each in Bolsa Bay, Santa Monica Bay, and off Point Loma to 157 ppm dw near a Newport Bay shipyard sampled in 1972. Regional medians ranged over 1,800-fold from 0.04 ppm dw for Bolsa Bay in 1978-80 and the Oxnard coastal shelf in 1971, to 73.9 ppm dw collectively for shipyard sites in Newport Bay in 1972 (Table 9.1). The Newport shipyard area was, and continues to be, the most contaminated area surpassing the Palos Verdes shelf area by a factor of 12 in 1985-86. Mean concentrations in Los Angeles-Long Beach harbors, San Diego Harbor, and Marina del Rey were similar in the more recent years sampled. Bolsa and Upper Newport bays in 1979-80 were only one-tenth as high (0.04 and 0.006 ppm dw, respectively).
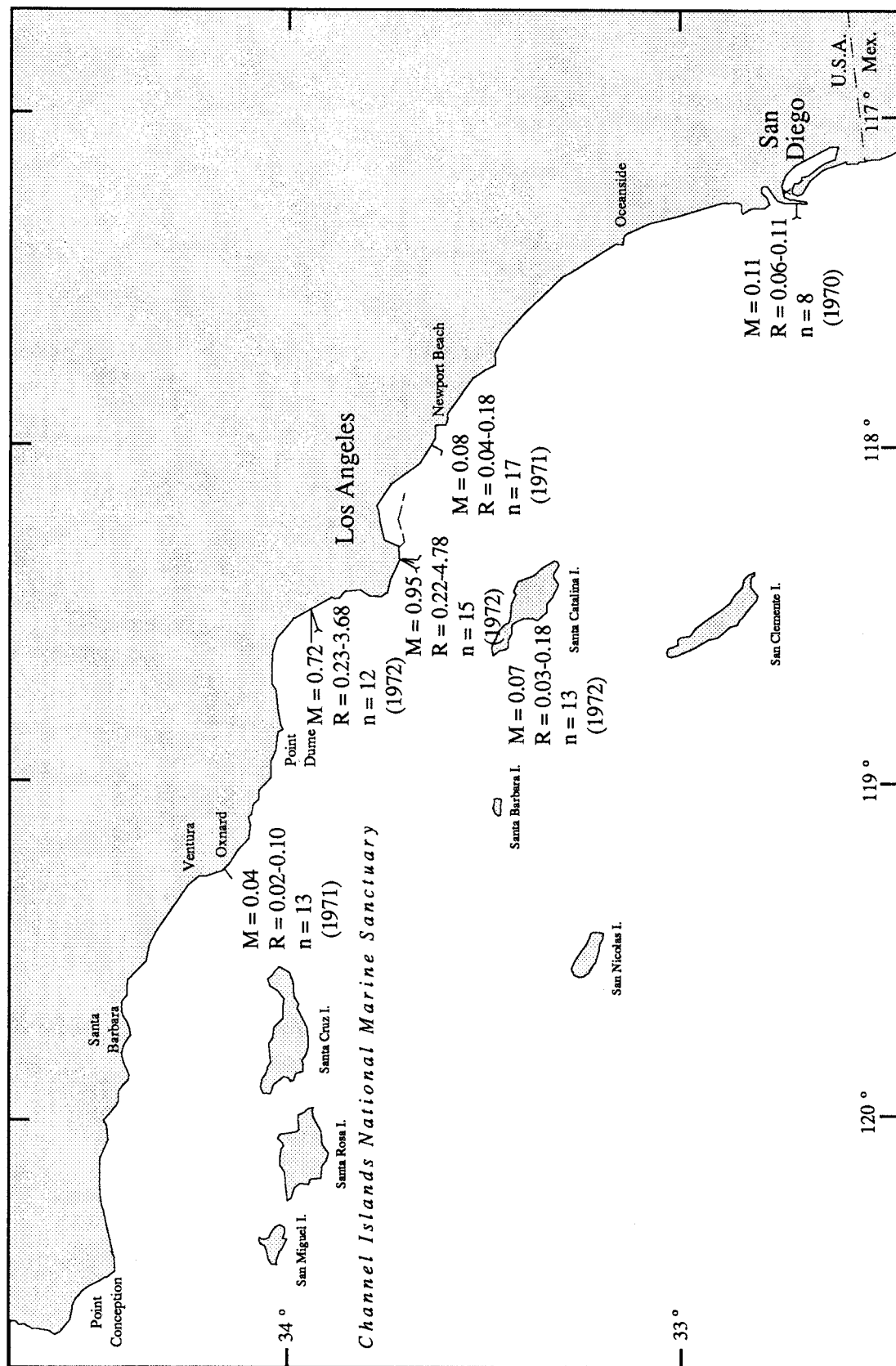
Figure 9.2. Median, range, and sample number values for total mercury (mg/dry kg) in surface sediments around five submarine outfalls and off Santa Catalina Island (after Eganhouse et al., 1976).

Table 9.1. Mean, median, minimum, and maximum mercury concentrations in surface sediment from selected surveys, 1970-86 in ppm dw.

SITE	Year	N	Mean	Median	Minimum	Maximum	Standard Deviation	Source
Outfall Areas:								
Oxnard shelf	1971[a]	13	0.04	0.04	0.02	0.10	0.03	1
Santa Monica Bay	1970[a]	16	0.18	0.17	0.01	0.42	0.12	2
	1971[a]	11	1.00	0.72	0.23	3.68	1.05	2
	1972[a]	20	0.72	0.44	0.05	5.90	1.24	2
Palos Verdes shelf	1972[b]	4	2.22	2.31	0.84	3.42	1.07	2
	1973[b]	10	3.77	2.9	1.87	8.45	2.11	2
	1985[b]	10	0.97	0.85	0.47	1.99	0.54	3
Orange County shelf	1985[b]	9	0.06	0.05	0.02	0.16	0.04	4
Point Loma shelf	1970[a]	10	0.10	0.11	0.02	0.16	0.05	1
	1971[a]	3	0.04	0.04	0.01	0.06	0.03	2
	1975[a]	17	1.46	0.69	0.05	6.52	2.04	2
Bays and Harbors:								
Marina del Rey[a]	1977	11	1.21	1.43	0.35	2.43	0.72	5
	1978	11	1.06	1.27	0.28	1.89	0.56	5
	1984	12	0.85	0.66	0.27	1.64	0.47	6
	1985	12	0.65	0.67	0.09	1.26	0.39	7
	1987	13	0.58	0.50	0.05	1.47	0.41	8
Los Angeles-Long Beach harbors [a]								
	1973	31	0.73	0.62	0.08	1.77	0.45	9
	1978	18	0.66	0.45	0.05	3.41	0.80	10
Bolsa Bay	1979-80	6	0.03	0.04	0.01	0.05		13
Upper Newport Bay	1971	3	0.11	0.11	0.03	0.12	0.07	14
Upper Newport Bay[a]	1980	8	0.06	0.06	0.03	0.09	0.02	11
Lower Newport Bay	1971	7	3.44	1.5	0.78	11.9	3.97	14
Newport shipyards	1972	9	73.9	70.0	19.0	157	50.8	15
Newport shipyards	1980	9	14.1	9.0	7.0	37.0	9.7	15
Newport shipyards	1986	6	11.8	11.3	8.4	19.0	4.0	15
San Diego Harbor	1971	11	5.8	3.92	1.65	17.95	5.06	14
San Diego Harbor[a]	1984	20	0.74	0.80	0.08	4.54	0.98	12
OVERALL					**0.01**	**157**		

[a] - all depths; [b] - 60-m only

1 SCCWRP, 1973	6 Soule and Oguri, 1985	11 MBC and SCCWRP, 1980
2 Eganhouse et al., 1976	7 Soule and Oguri, 1986	12 Ladd et al., 1984
3 Hyperion Treatment Plant, original data	8 Soule and Oguri, 1987	13 Feldmeth, 1980
4 CSDOC, original data	9 Chen and Lu 1974,	14 Young et al., 1975
5 Soule and Oguri, 1980b	10 Soule and Oguri, 1980a	15 Liu and Schneider, 1988

Available data led Eganhouse et al. (1976) to conclude background level of mercury in sediments of the shelf of the Bight are about 0.05 ppm dw. By this measure, most coastal shelf sites sampled in the past approached background within a factor of 10. Many bay and harbor sites have exceeded this reference by factors of 100 to more than 10,000.

Along the open coastal shelf, sediments from urban areas contained more mercury than those from more rural sites. Compared to the median of 0.07 ppm dw for 15 sites at Santa Catalina Island sampled in

1972, surface sediments from the Palos Verdes shelf (1972) and Santa Monica Bay (1976) were higher by factors of 10 or more (0.95 and 0.72 ppm dw). The Point Loma (1970) and Orange County (1971) shelves were comparable (0.11 and 0.08 ppm dw, respectively) and the Oxnard shelf (1971) was lower (0.04 ppm dw). Thus, bays (harbors) and coastal shelves of the Bight experienced order-of-magnitude subregional differences in sediment mercury contamination at some time during the period 1970-87, with gradients across individual regions ranging as high as 2 to 4 orders of magnitude.

Data from the 1986 NOAA NS&T Mussel Watch surveys and 1984 and 1985 Benthic Surveillance parallel the historical observations. Concentrations at 10 NS&T Mussel Watch sites ranged from 0.016 ppm dw at a 33-m deep site off Point Santa Barbara to 0.407 ppm near the Cabrillo Beach boat ramp in outer Los Angeles Harbor. Concentrations from the 1984-85 NOAA NS&T Benthic Surveillance sites ranged from less than 0.02 ppm dw at one inshore site in central Santa Monica Bay to 1.08 ppm dw at a site in central San Diego Harbor (Figure 9.2). These are all in the same range as historical concentrations at or near the NS&T sites; but, the historical data reached higher maxima in Los Angeles-Long Beach harbors (3.41), San Diego Harbor (4.54), Santa Monica Bay (3.68), and on the Palos Verdes shelf near San Pedro (8.45 ppm dw; Table 9.1). As shown in Figure 9.3, concentrations in several harbor areas were greater than 0.5 ppm dw (San Diego Harbor and Los Angeles-Long Beach harbors areas). Except at Palos Verdes, shelf site concentrations were in the range 0.03 to 0.2 ppm dw (Santa Barbara, Santa Monica Bay, and coastal sites between Newport Beach and Point Loma).

It is possible natural mercury concentrations increase with depth in a fashion similar to other metals. However, no surveys have been conducted to confirm this. The 1969-71 Santa Barbara Basin surface layer concentration of approximately 0.12 ppm dw (Young et al., 1973) was higher by a factor of 3 than the median of 0.04 ppm dw for 1972-collected Oxnard shelf samples. This may reflect higher mercury concentrations in fine deepwater silts and clays than in the fine sand typical of the Oxnard shelf. However, in the absence of cross-shelf or deepwater sediment surveys for mercury, it is difficult to confirm with certainty that sediment concentrations increase with depth.

Organic mercury was measured in sediments from one region--the Palos Verdes shelf--during 1975 (Eganhouse et al., 1978). Concentrations were rather constant, at 0.005 ppm dw across the shelf at 30, 150, and 300 meters, while total mercury ranged from about 0.3 to over 5.0 ppm dw. As a consequence, the organic mercury fraction ranged from less than 0.1 to about 2 percent of the total, with the highest percentage at the sites least contaminated with total mercury. However, along the 60-m isobath (depth of sewage discharge), organic mercury concentrations were highest (up to 0.021 ppm dw or about 0.5 percent of the total mercury) at sites on either side of the Whites Point outfall. Eganhouse et al. (1978) explained the low value (0.007 ppm dw) at the outfall as coinciding with areas of high sulfide concentration. Since surveys have not been extended beyond Palos Verdes, it is not possible to determine what the natural ratio of organic and total mercury should be in the Bight.

The toxicity of the sediment concentrations found in the Southern California Bight is uncertain. Swartz et al. (1988) estimated an amphipod LC_{50} of mercury (total) at 13.1 ppm dw in sediments amended with mercuric chloride. As seen from Table 9.1, no coastal shelf sediment contained levels above 13.1 ppm dw; but, a number of samples from near Newport Bay shipyards and from San Diego Bay did exceed this level. Swartz et al. (1988) also found that mercury, when combined with other chemicals in sediments, increased sediment toxicity but at less than additive concentrations. Finally, they also determined that mercury toxicity decreased with increasing organic matter in sediments. From a national review of sediment effects data, Long and Morgan (1990) calculated a probable effects range for mercury of 0.15 to 1.3 ppm dw (ER-L to ER-M). The lower of these concentrations was exceeded by median levels of mercury in sediments from all outfall areas except the Oxnard shelf and all bays and harbors except Bolsa Bay. The ER-M value was exceeded by recent measurements at Palos Verdes, Marina del Rey, and Newport Bay.
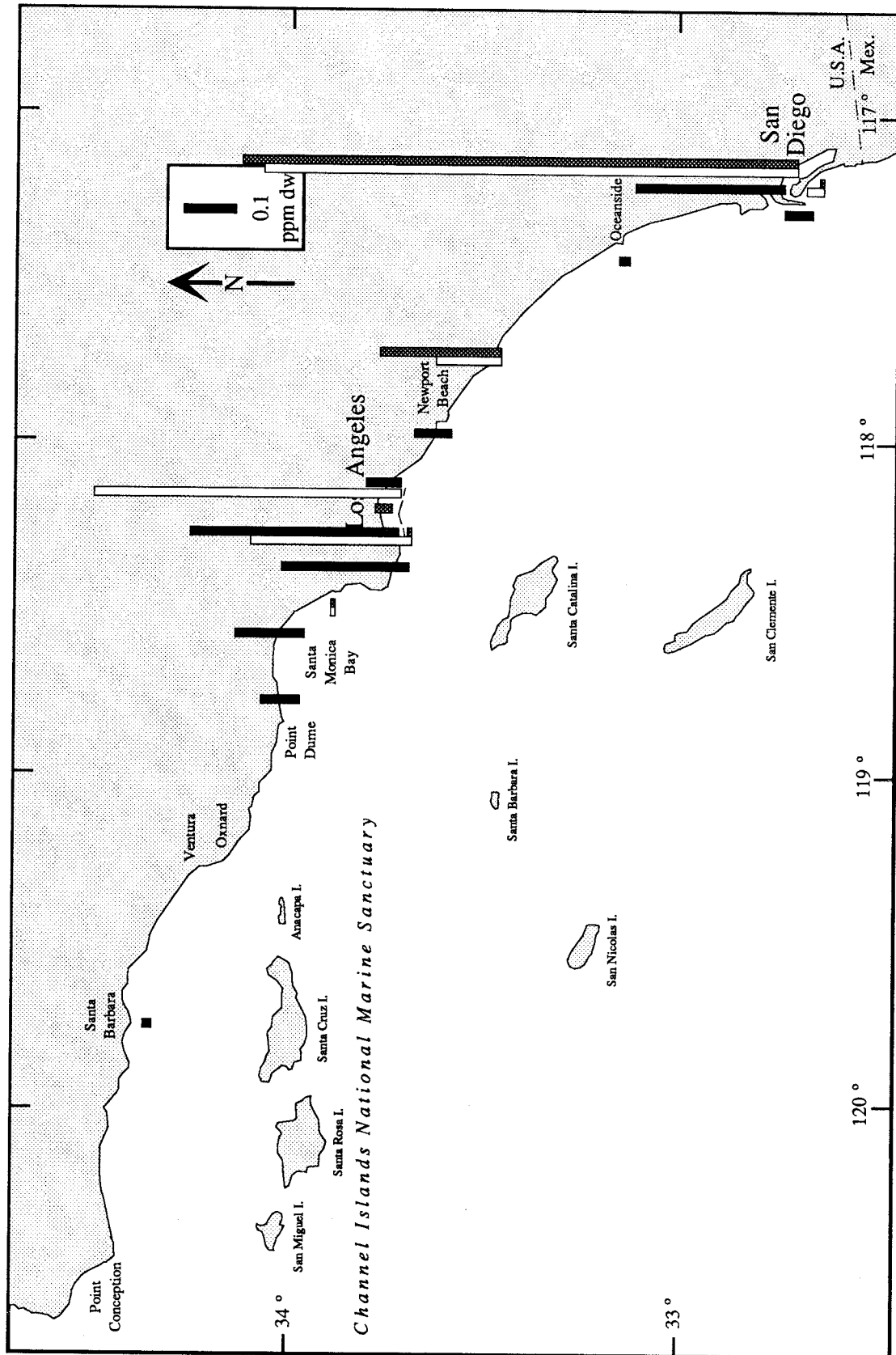
Figure 9.3. Mercury concentrations in the surficial sediments of the Southern California Bight based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 (▯) and 1985 (▮) and Mussel Watch Project for 1986 (▮) (NOAA, unpublished data and NOAA, 1988).

Measurements in dated sediment cores collected between 1968 and 1971 from a 580-m deep site in the Santa Barbara Basin indicated that total mercury concentrations have doubled during the past century. They have increased from about 0.06 ppm dw during the mid-19th century, then varied between 0.08 and 0.10 ppm dw between 1890 and 1949, then increased sharply to 0.16 ppm dw during the 1960s (Young et al., 1973). In very deep layers, dated to approximately 1500 years ago, mercury concentrations were about 0.04 ppm dw. There are no recently collected cores from this or other offshore region from which it is possible to determine if concentrations continued to increase, level off, or decrease during the 1970s and 1980s. However, it is clear from several data sets that there has been a dramatic decrease of mercury contamination in sediments along the Palos Verdes shelf. Between 1972 and 1975, surface sediment concentration decreased about 15 percent based on surveys conducted by SCCWRP (Eganhouse et al., 1976). Based on additional surveys conducted by CSDLAC, mean surface sediment concentrations along the 60-m isobath in this region decreased 69 percent from 3.24 ppm dw in 1974 to 1.01 ppm dw in 1985 (Figure 9.4). Thus, mercury in surface sediment at Palos Verdes has decreased by 71 percent between 1971 and 1985. These dramatic declines are consistent with the long-term reductions in mercury emissions from the Whites Point outfall.
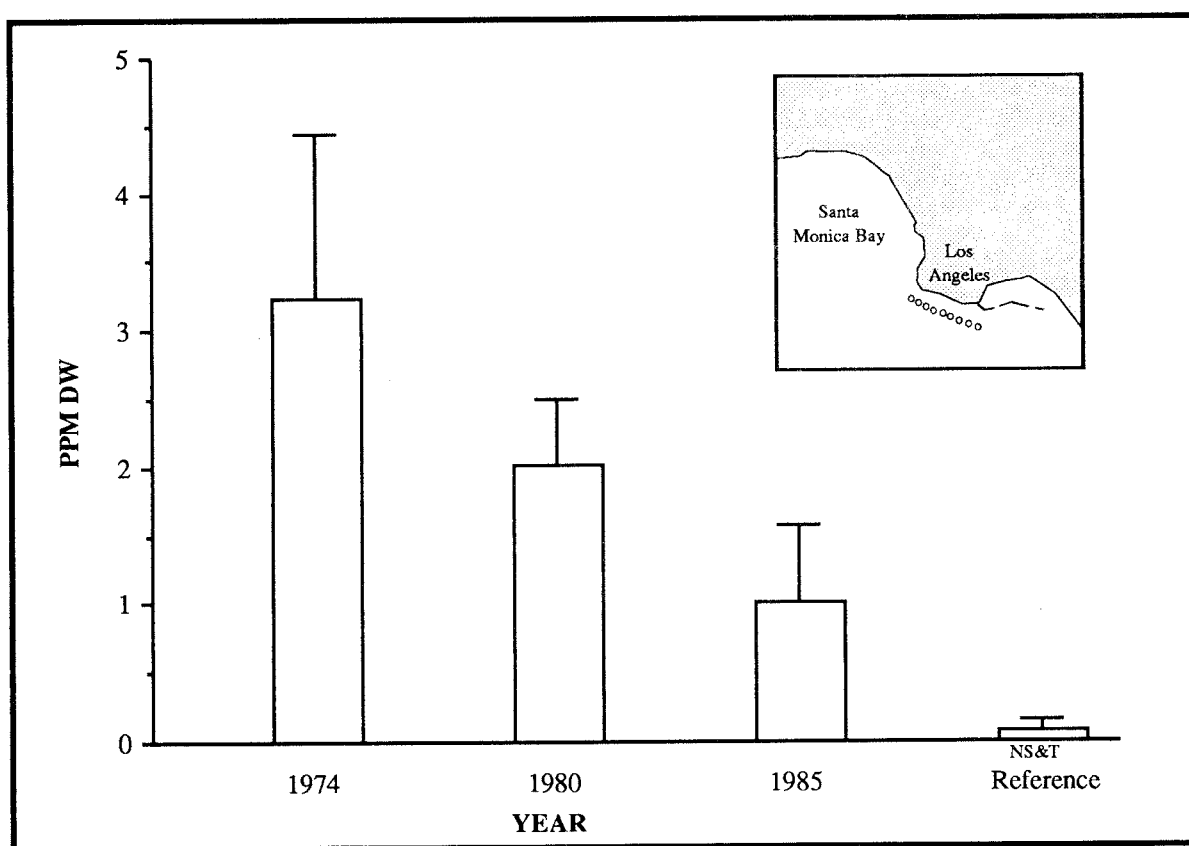
Figure 9.4. Mean mercury concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC. The reference value is based on the mean of four relatively isolated NOAA NS&T Program sites in the Southern California Bight sampled between 1984 and 1986 (NOAA, 1988 and unpublished data). Inset shows approximate locations of sites sampled by CSDLAC.

In summary, mercury has been elevated in sediments from Newport Bay shipyards, other bays and harbors, and outfall areas. It appears that mercury concentrations in sediment have decreased since 1971.

MERCURY IN MUSSELS

Mercury has been measured in mussels of the Bight in several regionwide synoptic surveys. Eganhouse and Young (1976) sampled *M. californianus* in 1974, CMW sampled *M. californianus* and *M. edulis* in 1977-78 (Stephenson *et al.*, 1979b), and the NS&T Program Mussel watch have sampled *M. edulis* and *M. californianus* annually since 1986 (NOAA, 1989). In addition, mercury was measured in many CMW samples between 1977 and 1986. The 1974 SCCWRP survey analyzed mercury in composites of digestive gland, adductor muscle, and gonad. Determinations in the CMW surveys were for whole soft tissue less gonad and the NS&T Mussel Watch survey analyzed composites of whole soft tissue.

Results for the 1974 survey from Eganhouse and Young (1976) and Eganhouse (unpublished) were reported as wet weight concentrations. Of the three organs surveyed, digestive gland had the highest concentrations and widest variations. Levels of mercury in digestive gland of *M. californianus* ranged over an order of magnitude, from 0.011 ppm ww at Gaviota Pier in Santa Barbara County, to 0.181 ppm ww at Sunset Cliffs Beach near the entrance to Mission Bay, San Diego County (Figure 9.5). The 17-site median was 0.056 ppm ww. There was no obvious coast or island gradient such as noted for lead. The mean concentration from five sites along the Santa Barbara coast (Gaviota to Port Hueneme) was similar to the mean concentration for the five island sites (0.044 and 0.046 ppm ww, respectively) as well as similar to four sites along the south coast between Newport Pier and Encinitas (0.037 ppm ww). However, the mean for two Palos Verdes sites (Royal Palms and Point Vincente) was about three times higher (0.136 ppm ww) and for two Santa Monica Bay sites (Point Dume and Santa Monica Pier) about twice as high (0.076 ppm ww). Thus, two areas of elevated digestive gland mercury stood out: the vicinity of the Palos Verdes Peninsula and the coast near Mission Bay, where the highest concentration (0.181 ppm ww) was recorded.

During the two 1977 CMW surveys when whole *M. californianus* (less gonads) were measured at 13 sites in the Bight, highest mean concentration of mercury occurred at the west end of San Miguel Island (0.48 ppm dw), at Royal Palms (0.23 ppm dw), and at La Jolla (0.20 ppm dw; Table 9.2). However, no significant difference was obtained using the Mann-Whitney test (Zar, 1984) between the mean concentration for seven coastal sites and six island sites (as classified in Table 9.2). Thus, there was no apparent regionwide gradient of mercury contamination, a conclusion in full agreement with the 1974 synoptic survey (Eganhouse and Young, 1976) and subsequent surveys (see below).

Table 9.2. Mean concentrations of mercury, ppm dw, in whole soft tissue (less gonads) of *M. californianus* from seven coastal (C) sites and six island (I) sites in the Southern California Bight sampled during winter and summer, 1977 (Phillips, 1988).

Site	Classification	Mean
San Miguel Island (west)	I	0.484
Royal Palms	C	0.229
La Jolla	C	0.202
Corona del Mar	C	0.199
Point Conception	C	0.134
Santa Catalina Island (west)	I	0.133
Anacapa Island	I	0.100
Point Conception	C	0.100
Santa Barbara Island	I	0.090
San Miguel Island (east)	I	0.086
Santa Cruz Island	I	0.070
Point Mugu	C	0.062
Oceanside	C	0.059
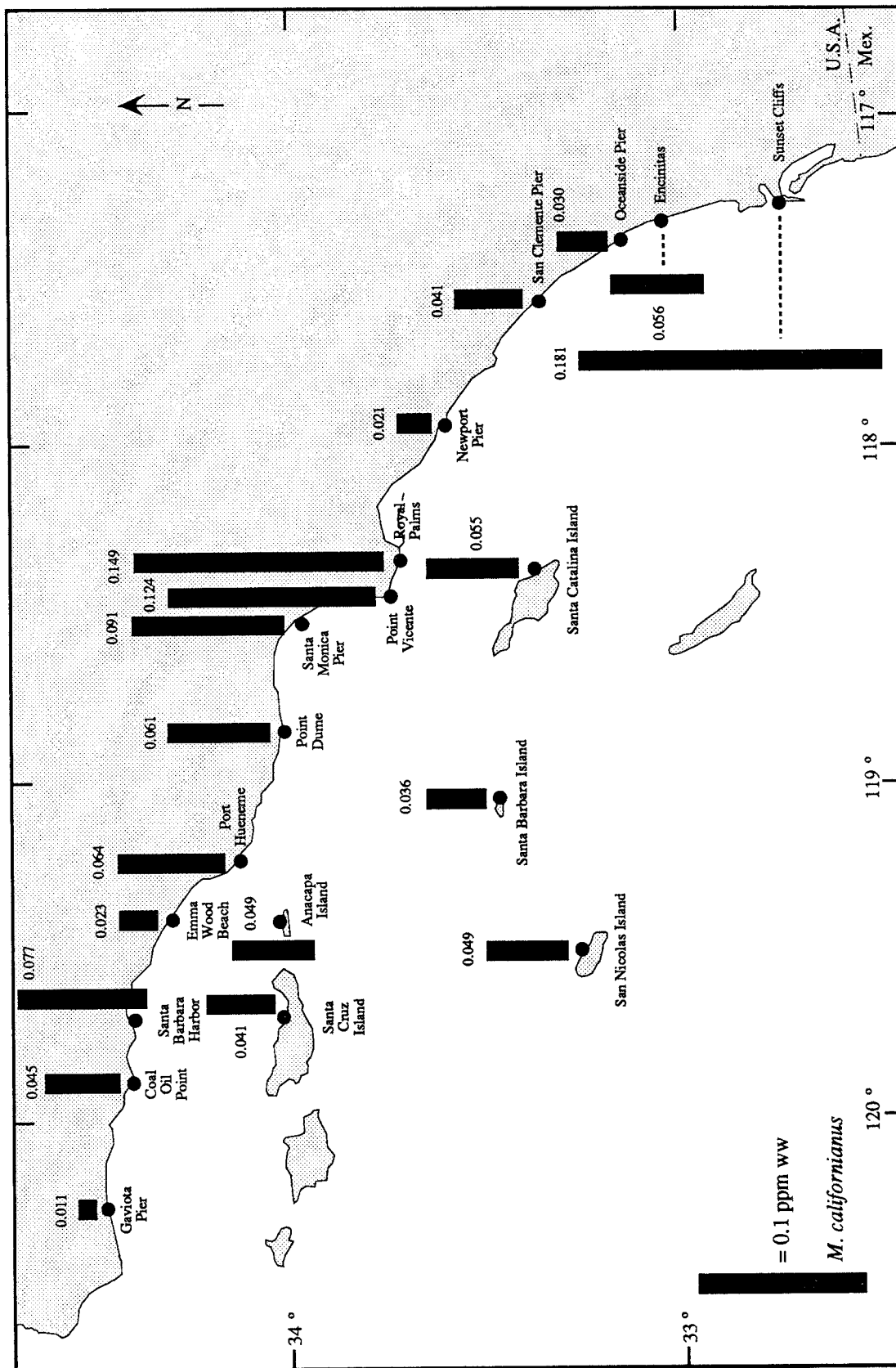
Figure 9.5. Concentrations of mercury measured in digestive gland tissue of mussels collected in the Southern California Bight in 1974. Sources: Eganhouse and Young (1976); Eganhouse, unpublished data.

Two survey activities conducted during 1982 and early 1983 provided a different perspective of possible large-scale gradients of mercury in mussels. While the CMW surveyed sites in northern, central, and southern California, Gutiérrez-Galindo and Flores-Muñoz (1986) sampled mussels at eight sites between Punta Bandera (near the United States-Mexico boundary) and San Quintin 275 km to the south. The mean concentration at 6 southern California coastal sites (0.144 ppm dw) was significantly lower (p≤ .05) than the mean concentrations at 4 northern California sites (0.379 ppm dw), 12 Monterey-area sites (0.328 ppm dw), 10 San Luis Obispo County sites (0.311 ppm dw), and the 8 Baja California sites (0.485 ppm dw). Although the highest 1982-83 mean levels in southern California *M. californianus* were recorded near sewage outfall sites at Point Loma (NOSC Dolphin tanks, 0.4 ppm dw) and at Royal Palms (0.254 ppm dw), the concentrations were similar to those for coastal areas to the north and south beyond the Bight.

Mercury concentration in ppm dw in whole soft body tissue from *M. californianus* in the 1986 NS&T Mussel Watch Project were highest at coastal promontory sites such as Point Loma (0.27), Point La Jolla (0.23), and Point Dume (0.16; Figure 9.6). The finding of elevated concentrations at Point Loma and La Jolla agrees with the results of Eganhouse and Young who also found high values in the same region 12 years earlier. However, the value at Royal Palms (0.13 ppm dw) was within the range of values from other coastal and island sites (0.08 to 0.17 ppm dw) excluding Point Loma and Point La Jolla.

Conditions within and among bays and harbors are difficult to assess. CMW sampled *M. californianus* from 11 sites within Santa Monica Bay in 1980. The range was relatively small, from 0.20 to 0.45 ppm dw with a mean of 0.30 (Table 9.3 and Figure 9.7). This compares with a mean of 0.27 ppm dw and a range of 0.01 to 1.30 ppm dw for the full set of southern California CMW results from 1977 to 1986. NS&T Mussel Watch analyzed mussels from one coastal and one harbor location in Santa Monica Bay. Because *M. californianus* was analyzed at Point Dume and *M. edulis* at Marina del Rey, direct comparisons are not possible. However, the mean concentration at Point Dume (0.16 ppm dw) was at the high end of the range for all *M. californianus* analyzed in the Southern California Bight by the NS&T Program in 1986 (0.06 to 0.27 ppm dw). Two of three measurements from *M. edulis* collected at Marina del Rey (0.06, 0.22, and 0.24 ppm dw) were the highest concentrations for that species in the Bight (site means, 0.13 and range of 0.07 to 0.019 ppm dw).

Table 9.3 Summary of mercury concentrations (ppm dw) in whole *M. californianus* from several sampling areas in the Southern California Bight (Phillips, 1988 and NOAA, 1989).

Region or Site	Year	N	Mean	Median	Min	Max	SD	Source
All CMW	1977-85	123	0.27	0.20	0.01	1.3	0.21	Phillips, 1988
Santa Monica Bay	1980	10	0.30	0.32	0.20	0.45	0.10	Phillips, 1988
Santa Catalina Island	1980	5	0.21	0.24	0.11	0.30	0.07	Phillips, 1988
Newport to Imperial Beach	1980	13	0.21	0.14	0.11	0.70	0.17	Phillips, 1988
Point Dume	1986	3r	0.16	0.16	0.14	0.19		NOAA, 1989
Santa Barbara Channel	1986	3	0.11	0.11	0.09	0.14		NOAA, 1989
All NS&T	1986	11	0.14	0.11	0.06	0.27		NOAA, 1989

Figure 9.6. Mercury in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.
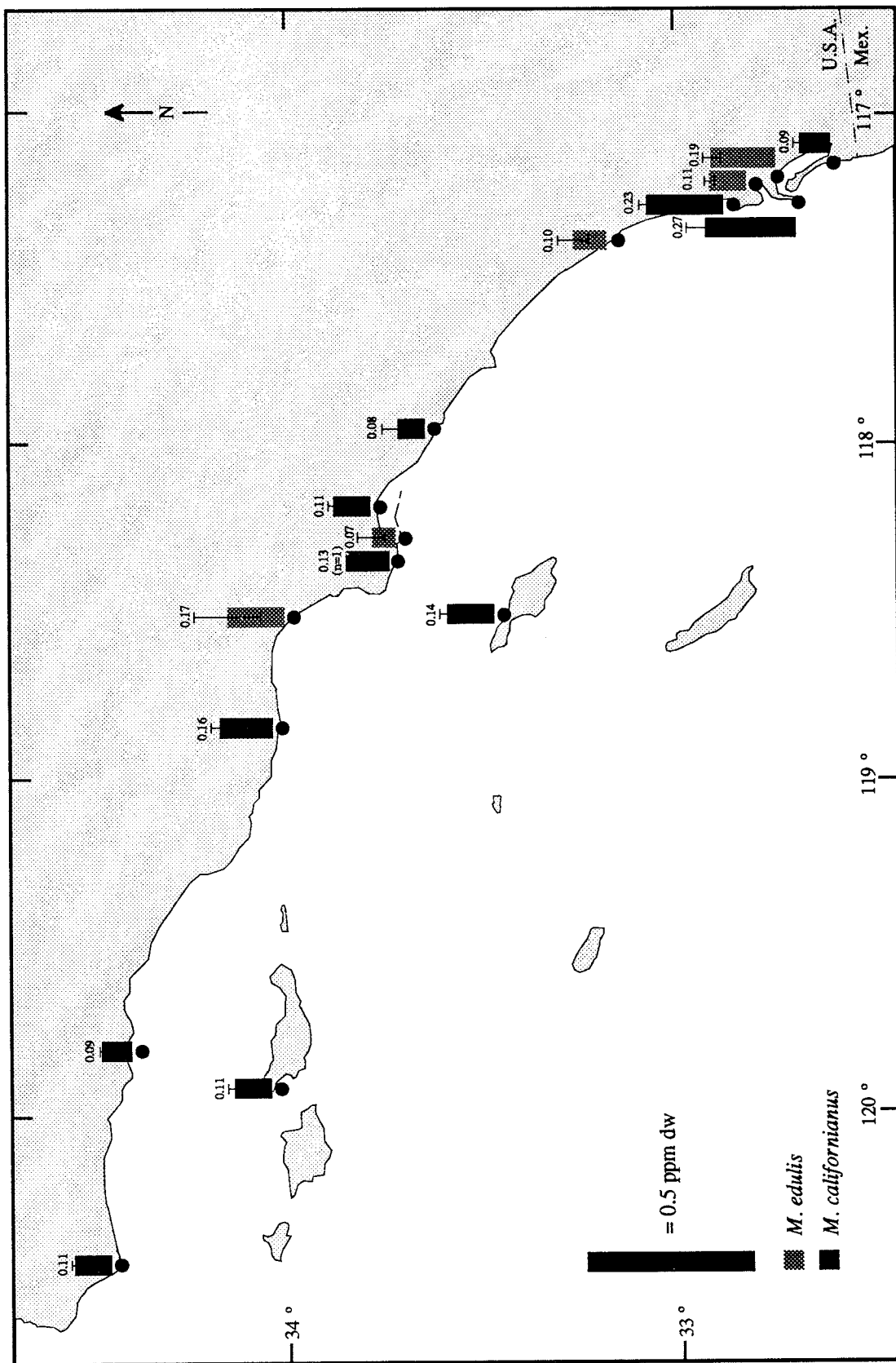
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Figure 9.7. Mercury in whole soft body tissue, less gonads, of mussels sampled in Santa Monica Bay in 1982. Source: Phillips, 1988.

The Los Angeles-Long Beach harbor complex is the only harbor area with a clear mercury gradient in mussels. Results from the CMW Program's 1982 and 1983 intensive surveys represent the largest number of measurements available from one program or study within Los Angeles-Long Beach harbors. Compared to a mean and range of 0.22 and 0.02 to 0.94 ppm dw for all southern California *M. edulis* analyzed in CMW (n = 39), 11 Los Angeles-Long Beach harbors sites had a mean and range of 0.19 and 0.02 to 0.44 ppm dw, respectively (Table 9.4). Results of surveys from 1982 suggested that there was a strong fivefold gradient of increasing mercury concentrations in *M. edulis* toward inner harbor sites (Figure 9.8). For example, concentrations in *M. edulis* at five outer harbor sites ranged from 0.02 to 0.18 ppm dw. The range was 0.09 to 0.27 ppm dw at six inner harbor sites. However, the persistence of this pattern and the location of mercury epicenters is in doubt when CMW data from other years are examined. For example, the lowest concentration (0.02 ppm dw) as well as one of the highest (0.40 ppm dw) were measured at the same location, the Los Angeles Harbor Tide Gauge, in two different years. The highest concentration in the region (0.44 ppm dw) was recorded in 1985 from a site at the Los Angeles River mouth just beyond the harbor complex.

A relatively small number of results are available for *M. edulis* from San Diego Harbor. CMW Program measurements at four sites sampled between 1980 and 1982 indicated that San Diego Harbor mussels were less contaminated by mercury than the mussels from many other areas surveyed. Both mussel species were collected and concentrations of mercury ranged from 0.21 to 0.25 ppm dw (Table 9.4). These concentrations are lower than the levels found by the same program of 1.30 ppm dw in *M. californianus* from Bird Rock (near La Jolla) in 1979 and 0.94 ppm dw in *M. edulis* at Oceanside Harbor in 1985. They are comparable to values from outer Los Angeles-Long Beach harbors.

In 1986, the NS&T Mussel Watch Project measured levels of mercury in *M. edulis* from Harbor Island in San Diego Harbor in the same range as those found by the CMW Program (Table 9.4). Concentrations ranged from 0.17 to 0.22 ppm dw (mean 0.19), which were near the high end of the range of southern California values for that species (station means, 0.07 to 0.19 ppm dw).

Table 9.4. Summary of mercury concentrations (ppm dw) in whole *M. edulis* from various sampling areas in the Southern California Bight 1980 through 1986 (Phillips, 1988 and NOAA, 1989).

Region or Site	Year	N	Mean	Median	Min	Max	S D	Source
All CMW	1980-85	39	0.22	0.20	0.02	0.94	0.17	Phillips, 1988
Channel Islands Harbor	1980	1	0.21					Phillips, 1988
Marina del Rey	1980	1	0.36					Phillips, 1988
Marina del Rey	1986	3r	0.17	0.22	0.06	0.24		NOAA, 1989
Los Angeles-Long Beach harbors	1982-85	17	0.19	0.18	0.02	0.44	0.13	Phillips, 1988
San Pedro breakwater	1986	3r	0.07	0.08	0.02	0.10		NOAA, 1989
Colorado Lagoon	1982,1985	3	0.35	0.27	0.20	0.60		Phillips, 1988
Anaheim Bay	1980,1982	2	0.18	0.18	0.12	0.23		Phillips, 1988
Newport Bay	1980,1985	4	0.23	0.19	0.13	0.45	0.13	Phillips, 1988
Newport Pier	1980	1		0.12				Phillips, 1988
Oceanside Harbor	1985	1	0.94					Phillips, 1988
Mission Bay	1980,1982	5	0.10	0.07	0.06	0.09	0.01	Phillips, 1988
Point Loma	1983	1	0.18					Phillips, 1988
San Diego Harbor	1980,1982	4	0.23	0.22	0.21	0.25	0.02	Phillips, 1988
San Diego Harbor Island	1986	3r	0.19	0.18	0.17	0.22		NOAA, 1989
All NS&T	1986	5	0.13	0.11	0.07	0.19	0.05	NOAA, 1989
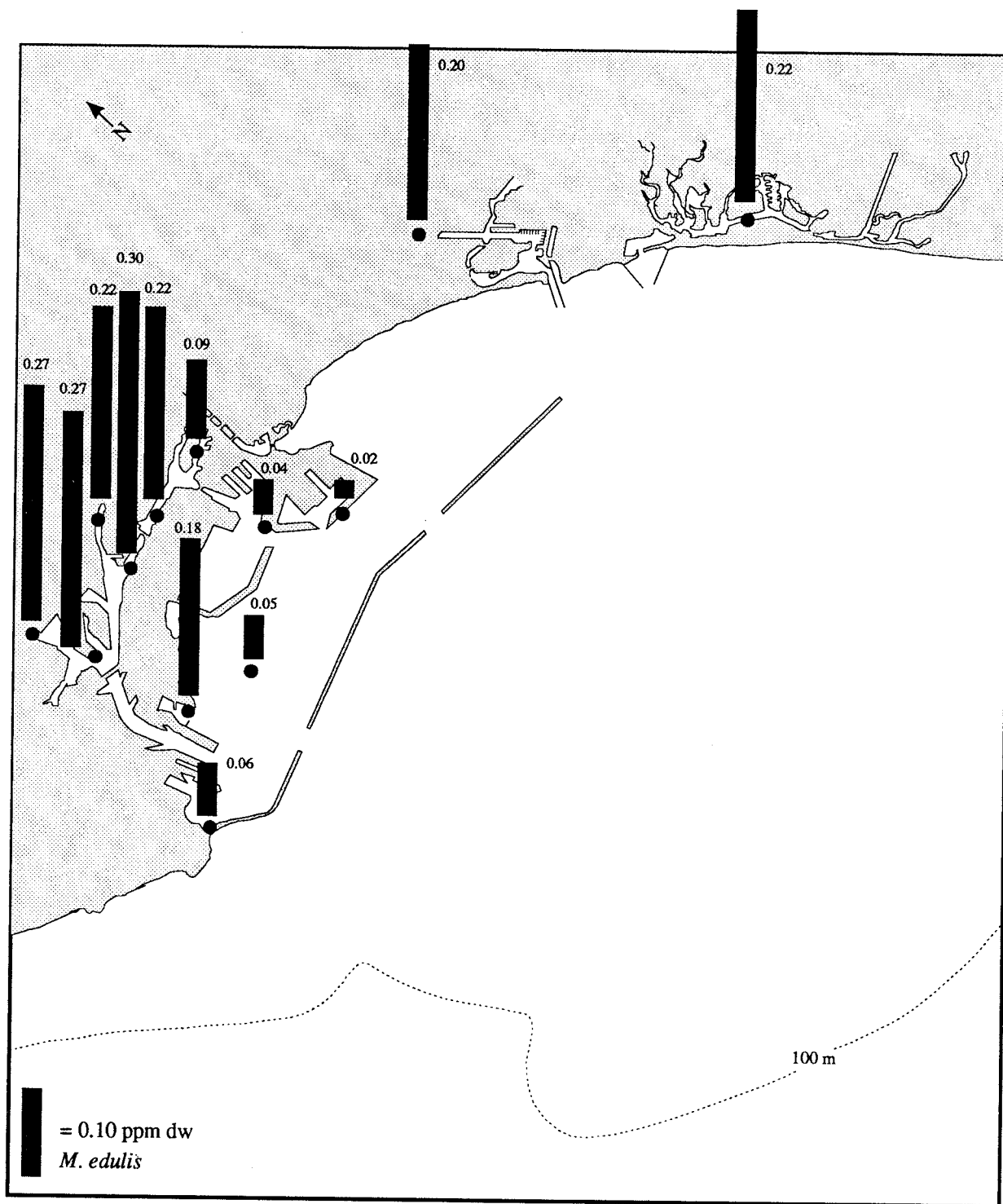
Figure 9.8. Mercury in whole soft body tissue, less gonads, of mussels sampled in San Pedro Bay in 1982. Source: Phillips, 1988.

In summary, it appears that there have been no strong or regionwide gradients of mercury in *M. californianus* indicative of major sources in the Los Angeles or San Diego areas. There is some evidence that mercury concentrations in *M. californianus* have actually been lower in the Southern California Bight than in central California or northern Baja California. Indeed, the 1986 distribution of mercury in *M. californianus* analyzed for the NS&T Mussel Watch Project is reminiscent of that found for cadmium and arsenic, where concentrations increase with distance from the Los Angeles area, and suggests that, now, oceanic physical processes could be of importance in determining body burdens of mercury in mussels. Recent research by Gill (1986) has demonstrated the presence of a mercury maximum in water at or near the thermocline in some regions. Eisler (1987) noted that upwelling and phytoplankton activity may significantly affect the global cycling of the element. Based on these observations, it is possible that coastal upwelling is now the major source of mercury-enriched water or food organisms, which may, in part, account for existing tissue levels of mercury in *M. californianus*. Locally, mercury was elevated in mussels at Royal Palms during the early 1970s and along the Point Loma coast during all survey periods. Further, there was evidence of elevated mercury levels (up to fivefold) in *M. edulis* from inner Los Angeles-Long Beach harbors, but apparently not for San Diego Harbor.

There are very few data from which to judge the direction and magnitude of long-term trends of mercury in mussels. Three sites for which time-series data from the CMW Program are available--Royal Palms State Park, Oceanside, and the west side of Santa Catalina Island--show a trend of increasing mercury concentrations from mid-1977 through 1979. Then, at each site, there appeared to be a marked decline after 1980 (Figure 9.9). Overall, there was no significant long-term increase or decrease at any of these sites. NOAA's NS&T Mussel Watch Program detected no significant changes in mercury concentrations at sites in southern California sampled since 1986 (NOAA, 1989).
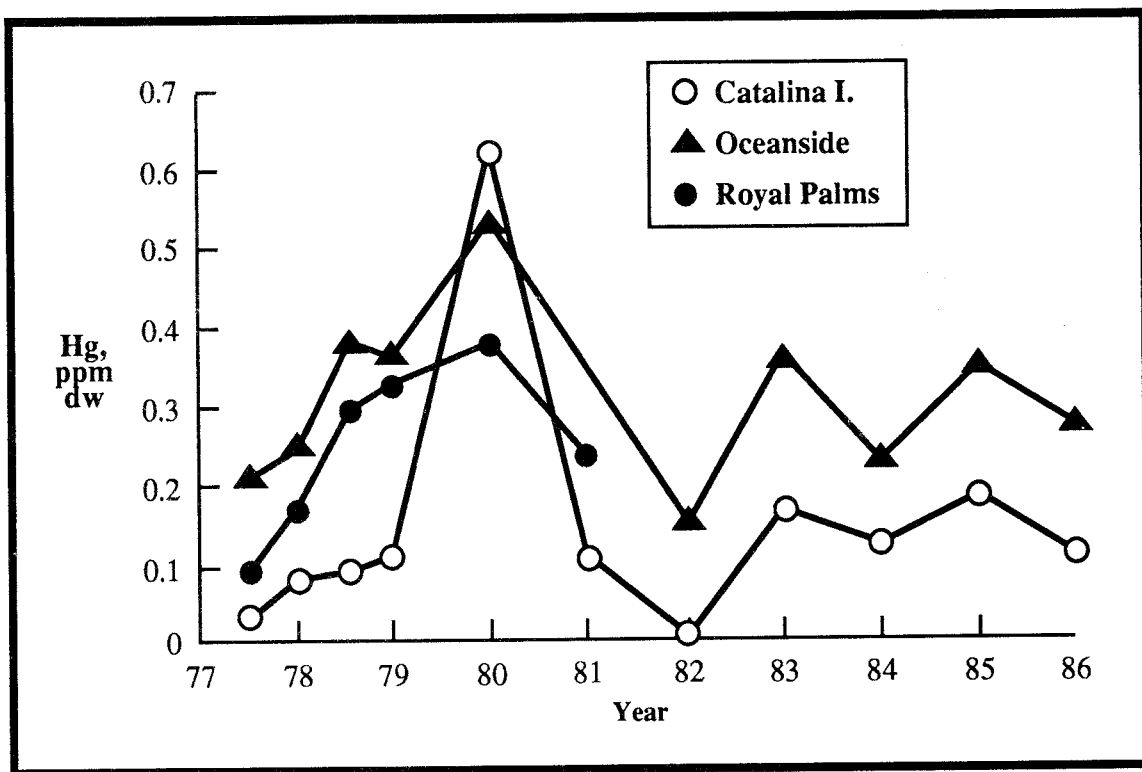
Figure 9.9. Temporal trend of mercury in *M. californianus* at three sites within the Southern California Bight, 1977-86, (Phillips, 1988).

A paucity of data on trends in mercury inputs precludes an assessment of the cause of variations in mercury content of mussels at all but one site. At Whites Point (Royal Palms), there was no significant correlation (p > 0.1) between variations in mercury mass emission rates from the JWPCP sewage outfalls and variations in mercury in mussels from the CMW Royal Palms site over the period 1977 through 1986. Thus, over this period of time, variations of mercury in mussels were unresponsive to variations in mercury in sewage that were, in fact, decreasing ($r^2 = 0.367$, p = 0.064). However, over a longer period (1974-86), there is indirect evidence that mercury concentration in mussels had been higher and may have decreased slightly in response to decreasing levels in the JWPCP sewage. Eganhouse and Young (1976) characterized municipal discharges as the predominant input route for mercury into the coastal waters of southern California. This is supported by the apparent spatial distribution of mercury concentrations found in their 1974 study. In 1974 concentrations of mercury in digestive glands of mussels from Palos Verdes were 3 times higher than in all non-urban and island areas. In addition, a study of mercury uptake in mussels suspended at various depths off Palos Verdes resulted in a threefold increase relative to initial concentrations at the control reference site at Point Sal. However, a time series was not conducted at the control site so it is not possible to confirm if the additional uptake at Palos Verdes was due to sewage inputs. In any case, in the 1986 NOAA NS&T Mussel Watch survey, mercury in whole Royal Palms mussels (0.13 ppm dw) was not as high as in digestive glands in 1974 (0.15 ppm dw), suggesting a possible decline over this period (mid-1970s to 1986).

An alternative possibility exists to explain these mercury trends. The similarity in temporal trends and levels between 1977 and 1980 at three sites of different physical and pollutant input characteristics (Figure 9.9) may suggest a large-scale and more diffuse input or inputs than would be expected if point sources such as municipal discharges were responsible. The importance of atmospheric deposition in determining distributions of other trace elements has been demonstrated, particularly for lead (see, for example, Alexander and Young, 1976). Gill (1986) noted that in some regions surface distributions of mercury are clearly similar to those for lead and lead isotopes. Also, because the latter are introduced to the ocean principally by way of atmospheric deposition, he suggested that atmospheric input is a significant influence on surface distributions and concentrations of mercury. Matheson (1979) observed that atmospheric transport of mercury may exist on a substantial scale because of the high volatility of the metal and its compounds. Major anthropogenic sources of mercury to the atmosphere include volatilization from manufactured goods (electrical equipment, paints, batteries, pesticides, pharmaceutical and dental uses) and the burning of fossil fuels, of which mercury is a trace constituent. Evidence that diffuse anthropogenic inputs of mercury have existed for many decades in the Southern California Bight was shown by dated marine sediments from a site well removed from discrete coastal anthropogenic inputs. Mercury concentrations began to increase in sediments after about 1900 and increased steadily through the 1960s.

An unusual source possibly influencing mercury distributions and trends in southern California mussels is suggested by Flegal et al. (1981). They noted elevated concentrations in M. californianus collected at two sites (Año Nuevo Island near Monterey and San Miguel Island) isolated from anthropogenic inputs and geological sources. However, the sites were close to large populations of pinnipeds and marine birds. Relatively high mercury concentrations found in fecal material of those organisms indicate that excreta from higher animals, which are known to accumulate and eliminate mercury, may be an important non-point source into the marine environment in some locations. Table 9.5 lists the 20 highest concentrations of mercury found among M. californianus analyzed in the CMW Program. At least nine of these sites where elevated levels were measured are frequented on a regular basis by pinnipeds such as the northern sea lion (Eumetopias jubata), harbor seal (Phoca vitulina), northern fur seal (Callorhinus ursinus), California sea lion (Zalophus californianus), Guadalupe fur seal (Arctocephalus townsendi), and northern elephant seal (Mirounga angustirostris) or were adjacent to confined marine mammals (NOSC dolphin tanks, Point Loma). As many as 500 harbor seals haul out at Point Conception, which produced the second highest concentration of mercury in M. californianus.

In summary, there have been no significant long-term increases or decreases of mercury concentration in mussels at the few sites where repeated measurements have been made. The interannual variations that did occur at Whites Point (Royal Palms) were unrelated to variations of mercury mass emission rates from sewage effluent. Other sources of temporal variations in mussels could include atmospheric fallout, interannual variations in upwelling, and haul out episodes of seals or sea lions that may defecate mercury-laden feces near some sites.

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Table 9.5. Top 20 ranked concentrations of mercury in soft body tissue (less gonads) of southern California *M. californianus* from CMW Project. Phillips, 1988.

Site	Sample Date	Proximity to mammal site	Tissue Hg, ppm dw
Bird Rock (La Jolla)	11/1/79		1.30
Point Conception	11/30/78	x	1.13
Royal Palms State Park	11/3/79		0.98
Whites Point	10/29/79		0.79
Royal Palms State Park	12/14/80		0.75
San Miguel Island	8/15/78	x	0.74
NOSC dolphin tanks (Point Loma)	12/13/80	x	0.70
Oceanside	10/28/79		0.62
NOSC dolphin tanks (Point Loma)	1/3/83	x	0.60
Cabrillo Beach (Los Angeles Harbor)	11/3/79		0.54
Royal Palms State Park	10/30/79		0.53
San Miguel Island	11/18/78	x	0.50
Point Loma	12/26/85	x	0.50
Palos Verdes	11/3/79	x	0.47
Point Dume	12/11/80		0.45
La Jolla-	10/31/79		0.45
San Miguel Island	12/3/77	x	0.44
Santa Catalina Island	12/13/79	x	0.43
Corona del Mar (Newport)	10/27/79		0.41
El Segundo (Santa Monica Bay)	12/11/80		0.39

MERCURY IN FISH AND OTHER SPECIES

Total mercury has been measured in about 900 samples or composites of at least 45 taxa of marine organisms from the Southern California Bight. Table 9.6 summarized data for about 500 specimens including 5 species of crustaceans, 6 mollusks, 1 echinoderm, 6 shark species, 3 plants, 2 mammals, and 22 species of fish. "Organic" mercury content has also been determined for some of these (Eganhouse and Young, 1978). Most of the samples were taken as part of a 1975-77 seafood survey (Young *et al.*, 1978) and a study of pollutant biomagnification in marine food webs (Schafer *et al.*, 1982; Eganhouse and Young, 1978).

Mercury concentrations range over 8000-fold in marine life of the Bight. Concentrations of total mercury in non-hepatic tissues have ranged from 0.001 ppm ww in whole samples of sea lettuce (*Ulva*), collected in 1980 from a site in upper Newport Bay (MBC and SCCWRP, 1980) to 8.15 ppm ww in muscle of a white shark captured near Santa Catalina Island in 1980 (Schafer *et al.*, 1982; Table 9.6). Concentrations in liver have ranged from 0.014 ppm ww in a collection of hornyhead turbot from Santa Monica Bay to 2.82 ppm ww in a collection of barred sandbass from Dana Point (Varanasi *et al.*, 1989).

Highest mercury concentrations were in five of the six shark species sampled from the San Pedro-Santa Monica basin area in 1980-81. While the mean value was 0.096 ppm ww in a plankton-feeding basking shark (*Cetorhinus maximus*), concentrations in carnivorous sharks were: 0.661 in thresher shark (*Alopias vulpinus*), 0.71 in blue shark (*Prionace glauca*), 1.44 in mako shark (*Isurus oxyrinchus*), 1.53 in spiny dogfish, and 8.1 in the white shark (Table 9.6). The highest concentrations in muscle of bony fish were 2.6 ppm ww in a composite of swordfish from Santa Catalina Island in 1980 followed by 0.383 in a composite of Pacific barracuda (*Sphyraena argentea*) from off Newport Beach. All invertebrates sampled contained low concentrations (0.6 ppm ww or less).

Table 9.6. Mercury (ppm ww) in edible tissues of marine organisms from the Southern California Bight.

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum Mercury	Maximun Mercury	Standard Deviation	Source
Algae (Entermorpha, whole)	Newport Bay	1980	5	0.004	0.004	0.001	0.006	0.002	MBC and SCCWRP, 1980
Algae (Ulva, whole)	Newport Bay	1980	5	0.047		0.032	0.056		MBC and SCCWRP, 1980
Kelp (stipe)	Los Angeles Harbor	1979	5	0.008	0.009	0.003	0.010	0.003	Young and Mearns, 1980
Mysids (whole)	Palos Verdes	1981	5	0.006	0.007	0.003	0.009	0.002	Young and Mearns, 1980
Zooplankton (whole)	Santa Catalina Island	1980	3	0.020	0.017	0.003		0.015	Schafer et al., 1982
Green urchin (gonad)	Palos Verdes	1975	3	0.021	-	0.020	0.024	0.002	Eganhouse and Young, 1978b
Black abalone (foot)	Palos Verdes	1975-77	6	0.011	0.011	0.007	0.018	0.004	Young et al., 1978
	Dana Point	1975-77	5	0.010	0.010	0.009	0.012	0.002	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.006	0.008	0.001	0.009	0.004	Young et al., 1978
	San Clemente Island	1975-77	6	0.023	0.010	0.004	0.062	0.025	Young et al., 1978
Snail (viscera)	Palos Verdes	1975	8	0.071	-	0.026	0.124	0.041	Eganhouse and Young, 1978b
Snail (foot)	Palos Verdes	1975	8	0.005	-	0.002	0.012	0.004	Eganhouse and Young, 1978b
Gaper clam (neck)	Los Angeles Harbor	1979	5	0.023	0.025	0.015	0.028	0.005	Young and Mearns, 1980
Sea slug	Palos Verdes	1975	23	0.015	-	0.002	0.030	0.012	Eganhouse and Young, 1978b
Purple-hinge scallop	Palos Verdes	1975-77	3	0.059	0.056	0.053	0.069	0.009	Young et al., 1978
	Laguna Beach	1975-77	3	0.025	0.024	0.018	0.032	0.007	Young et al., 1978
	Santa Catalina Island	1975-77	2	0.028	-	0.013	0.042	0.021	Young et al., 1978
	Cortez Bank	1975-77	1	0.025	-	-	-	-	Young et al., 1978
Market squid (mantle)	Santa Catalina Island	1979	3	0.026	0.025	0.017	0.035	0.009	Schafer et al., 1982
	Palos Verdes	1975-77	3	**0.078**		0.078	0.150		Young et al., 1978
	Santa Catalina Island	1975-77	10	**0.054**		0.031	0.078		Young et al., 1978
Ridgeback prawn	Palos Verdes	1980	3	0.072	0.071	0.006	0.082	0.010	Schafer et al., 1982
	San Pedro Bay	1975-77	10	0.039	0.040	0.026	0.051	0.007	Young et al., 1978
	Dana Point	1975-77	10	0.052	0.046	0.023	0.089	0.025	Young et al., 1978
	Palos Verdes	1975	24	0.038	-	0.017	0.057	0.011	Eganhouse and Young, 1978b
California spiny lobster	Point Dume	1975-77	2	0.283	-	0.276	0.290	0.010	Young et al., 1978
	Laguna Beach	1975-77	6	0.305	0.284	0.208	0.484	0.098	Young et al., 1978
	San Diego Coast	1975-77	1	0.092	-	-	-	-	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.277	0.250	0.197	0.383	0.096	Young et al., 1978
Purple shore crab	Newport Bay	1980	3	0.068	0.074	0.053	0.078	0.013	MBC and SCCWRP, 1980
	Newport Bay	1980	5	0.047	0.049	0.032	0.056	0.010	MBC and SCCWRP, 1980
Pointer crab (digestive gland)	Palos Verdes	1975	11	0.030	-	0.011	0.042	0.010	Eganhouse and Young, 1978b
Pointer crab (digestive gland)	Santa Monica Basin	pre-1974	8	0.273		0.080	0.620		Fowler et al., 1974
Pointer crab (gonad)	Santa Monica Basin	pre-1974	8	0.321		0.013	0.137		Fowler et al., 1974
Pointer crab	Palos Verdes	1975	11	0.021	-	0.008	0.037	0.009	Eganhouse and Young, 1978b
Pointer crab	Santa Monica Basin	pre-1974	8	0.328		0.110	0.580		Fowler et al., 1974
Yellow crab	San Pedro Bay	1975-77	7	0.079	0.075	0.021	0.131	0.037	Young et al., 1978
	Dana Point	1975-77	3	0.103	0.071	0.068	0.171	0.059	Young et al., 1978
Northern anchovy	Newport Bay	1980	5	0.033		0.026	0.037		MBC and SCCWRP, 1980
	Coastal	1980	3	0.033	0.034	0.023	0.042	0.010	Schafer et al., 1982
	Los Angeles Harbor	1979	4	0.024	0.022	0.019	0.031	0.005	Young and Mearns, 1980
	Palos Verdes	1975-77	10	**0.077**		0.062	0.120		Young et al., 1978
	San Pedro Bay	1975-77	4	**0.078**		0.030	0.120		Young et al., 1978
	Santa Catalina Island	1975-77	10	**0.067**		0.022	0.120		Young et al., 1978
Pacific sardine	Santa Monica Bay	1980	4	0.046	0.047	0.035	0.052	0.007	Schafer et al., 1982
Jack mackerel	San Pedro Channel	1980	3	0.046	0.043	0.031	0.063	0.016	Schafer et al., 1982
Pacific mackerel	San Pedro Channel	1980	3	0.118	0.110	0.048	0.197	0.075	Schafer et al., 1982
Pacific hake	Newport	1980	3	0.108	0.091	0.062	0.170	0.056	Schafer et al., 1982
Pacific bonito	Various	1980	3	0.207	0.218	0.158	0.244	0.044	Schafer et al., 1982
	Palos Verdes	1975-77	3	**0.370**		0.270	0.380		Young et al., 1978
	San Pedro Bay	1975-77	7	**0.240**		0.120	0.450		Young et al., 1978
Bocaccio	Palos Verdes	1975-77	1	0.187	-	-	-	-	Young et al., 1978
	San Pedro Bay	1975-77	3	0.130	0.133	0.111	0.146	0.018	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.310	0.323	0.274	0.333	0.032	Young et al., 1978
Pacific barracuda	Newport/San Pedro Channel	1980	3	0.274	0.248	0.191	0.383	0.099	Schafer et al., 1982

Table 9.6. (continued)

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum Mercury	Maximun Mercury	Standard Deviation	Source
Swordfish	Santa Catalina Island	1980	5	2.180	2.200	1.790	2.600	0.309	Schafer et al., 1982
Topsmelt	Newport Bay	1978	3	0.054	0.051	0.049	0.062	0.007	Young and Mearns, 1980b
	Newport Bay	1980	5	0.049	0.049	0.033	0.057	0.010	MBC and SCCWRP, 1980
	Newport Bay	1980	5	0.038	0.038	0.030	0.047	0.006	MBC and SCCWRP, 1980
Striped mullet (adult)	Newport Bay	1980	5	0.016	0.018	0.011	0.019	0.003	MBC and SCCWRP, 1980
	Newport Bay	1980	5	0.015	0.014	0.012	0.023	0.005	MBC and SCCWRP, 1980
	Newport Bay	1978	3	0.014	0.010	0.010	0.022	0.007	Young and Mearns, 1980b
Striped mullet (young)	Newport Bay	1978	3	0.018	0.017	0.016	0.020	0.002	Young and Mearns, 1980b
Longjaw mudsucker	Newport Bay	1980	3	0.064	0.061	0.061	0.069	0.005	MBC and SCCWRP, 1980
	Newport Bay	1980	5	0.033	0.033	0.026	0.037	0.004	MBC and SCCWRP, 1980
Dover sole	Palos Verdes	1975	16	0.057	-	0.021	0.122	0.026	Eganhouse and Young, 1978b
	Palos Verdes	1980	3	0.046	0.047	0.041	0.049	0.004	Young and Mearns, 1980
Pacific sanddab	Palos Verdes	1975-77	4	0.085	0.081	0.080	0.097	0.008	Young et al., 1978
	San Pedro Bay	1975-77	10	0.113	0.111	0.083	0.190	0.032	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.094	0.072	0.053	0.156	0.055	Young et al., 1978
California halibut	Newport Bay	1980	5	0.040	0.021	0.026	0.077	0.035	MBC and SCCWRP, 1980
	Newport Bay	1980	5	0.090	0.091	0.059	0.130	0.027	MBC and SCCWRP, 1980
	Los Angeles Harbor	1979	4	0.088	0.086	0.073	0.108	0.018	Young and Mearns, 1980
	Palos Verdes	1975-77	3	0.283	0.253	0.240	0.357	0.064	Young et al., 1978
	San Diego Coast	1975-77	2	0.222	-	0.200	0.244	0.031	Young et al., 1978
California scorpionfish	Palos Verdes	1980	3	0.247	0.223	0.208	0.309	0.055	Young and Mearns, 1980
	Palos Verdes	1975-77	4	0.439	0.377	0.215	0.787	0.251	Young et al., 1978
	Dana Point	1975-77	10	0.817	0.249	0.028	5.490	1.656	Young et al., 1978
	Santa Catalina Island	1975-77	3	0.284	0.249	0.216	0.387	0.091	Young et al., 1978
White croaker	Los Angeles Harbor	1979	5	0.045	0.038	0.030	0.079	0.020	Young and Mearns, 1980
	Palos Verdes	1980	3	0.071	0.068	0.058	0.088	0.015	Schafer et al., 1982
	Palos Verdes	1975-77	3	0.144	0.048	0.039	0.344	0.174	Young et al., 1978
	San Pedro Bay	1975-77	3	0.185	0.175	0.174	0.205	0.018	Young et al., 1978
	Dana Point	1975-77	3	0.282	0.292	0.240	0.313	0.038	Young et al., 1978
Yellowfin croaker	Newport Bay	1978	3	0.055	0.050	0.048	0.066	0.099	Young and Mearns, 1980b
	Newport Bay	1980	5	0.070	0.072	0.048	0.093	0.017	MBC and SCCWRP, 1980
	Newport Bay	1980	5	0.037	0.035	0.032	0.047	0.006	MBC and SCCWRP, 1980
Kelp bass	Palos Verdes	1975-77	4	0.45		0.02	1.1		Young et al., 1978
	Orange County outfall	1975-77	10	0.36		0.120	1.100		Young et al., 1978
	Santa Catalina Island	1975-77	5	0.43		0.077	0.500		Young et al., 1978
Spotted sandbass	Newport Bay	1978	3	0.233	0.197	0.164	0.339	0.092	MBC and SCCWRP, 1980
Striped bass	Newport Bay	1978	3	0.295	0.278	0.238	0.369	0.067	MBC and SCCWRP, 1980
Basking shark	San Pedro	1980	1	0.096	-	-	-	-	Schafer et al., 1982
Blue shark	Palos Verdes	1980	4	0.710	0.668	0.446	1.065	0.270	Schafer et al., 1982
Mako shark	San Pedro Basin	1980	3	1.440	1.400	1.050	1.860	0.406	Schafer et al., 1982
Spiny dogfish	Palos Verdes	1981	5	1.530	1.680	0.980	1.760	0.319	Schafer et al., 1982
Thresher shark	Various	1980	5	0.661	0.682	0.361	0.845	0.188	Schafer et al., 1982
White shark	Santa Catalina Island	1980	3	8.100	8.030	5.680	10.600	2.461	Schafer et al., 1982

In the pelagic ecosystem, total mercury concentration in flesh or muscle of fish increased from the range of 0.03 to 0.07 ppm ww in planktivorous fish (northern anchovy, Pacific sardine, and jack mackerel) to 0.1 to 0.4 ppm ww in secondary carnivores (Pacific mackerel, Pacific hake, Pacific bonito, Pacific barracuda, and bocaccio) to about 2.2 ppm ww in swordfish (Schafer *et al.*, 1982). As noted above, concentrations in carnivorous sharks were also high (0.7 to 8.1 ppm ww). Similar evidence of mercury biomagnification occurred in a food web of Los Angeles Harbor (Mearns and Young, 1980) as well as in offshore ecosystems (Knauer and Martin, 1972).

Unpublished data sets may provide some understanding of the considerable inter-species variation in mercury concentrations. A brief review of data on mercury concentrations in over 300 samples of fish sampled by the CSDLAC between 1970 and 1974 yields slightly higher values than those published by Young *et al.* (1978), Eganhouse and Young, (1978), and Schafer *et al.* (1982) but similar inter-species differences. For example, the average mercury concentration in muscle of 42 Dover sole from Palos Verdes sampled between 1972 and 1974 by CSDLAC was 0.107 ppm ww (range 0.008 to 0.449). This agrees within a factor of 2 with a mean of 0.057 ppm ww (range 0.021 to 0.122) for Dover sole sampled from the same area in 1975 by Eganhouse and Young (1978). Both groups agree that kelp bass have had considerably higher concentrations. The mean for 29 fish sampled at Palos Verdes by CSDLAC between 1970 and 1974 was 0.746 ppm ww (range 0.04 to 2.35) compared to a mean of 0.45 ppm ww (range 0.02 to 1.1) for 4 fish sampled in 1975 in the same area by Young *et al.* (1978).

Hall *et al.* (1977) reported mean mercury concentrations of about 0.9 ppm ww (range 0.16 to 2.50) in spiny dogfish from Puget Sound and cite a mean of 0.6 in spiny dogfish off Oregon. Those values are comparable to the range of 0.98 to 1.76 ppm ww for five spiny dogfish from Palos Verdes (Table 9.6). Mean mercury concentrations in sablefish (*Anoplopoma fimbria*) from the northeast Pacific between the Bering Sea and San Diego ranged from 0.04 to 0.60 ppm ww with concentrations increasing downcoast toward San Diego (Hall *et al.*, 1976a). A similar gradient of increasing means (0.2 to 0.45) was observed in Pacific halibut from Kodiak Island, Alaska, to Washington (Hall *et al.*, 1976b). Thus, mercury gradients in the Bight may be part of a larger scale gradient affecting fish along the entire North American Coast.

Concern about mercury contamination in marine organisms in the Bight stems from observations by Klein and Goldberg that concentrations were highest in crabs, scallops, and whelk collected nearest the Hyperion sewage discharges in Santa Monica Bay and lowest in those from more distant sites. That may have been the case then (1969) and over the scale of area surveyed. However, more recent data do not demonstrate elevated concentrations of mercury in organisms taken at or near major mercury inputs. Eganhouse and Young (1978) found, that in spite of the excessive mercury contamination of sediment at Palos Verdes, tissue concentrations of both total and organic mercury were low. The concentrations were similar to those found for related animals at Santa Catalina Island and other parts of the world, and unrelated to the local sediment gradient. Further, mercury was measured in replicate composites of edible tissues from 14 popular seafood organisms in a 1975-77 effort to determine levels in animals taken near known major point sources, such as the Palos Verdes Peninsula. As shown in Table 9.7, total mercury concentrations were elevated over coastal or island reference site levels in only one species, purple-hinge scallop, from Palos Verdes. Concentrations were 0.059 ppm ww at Palos Verdes and 0.025 ppm ww near Laguna Beach, 0.028 ppm at Santa Catalina Island, and 0.025 ppm ww at Cortez Bank. For 13 other species, concentrations were either comparable among sites (as in Pacific sanddabs) or were lower at Palos Verdes than at other sites (in red sea urchins (*Strongylocentrotus franciscanus*) or white croaker; Table 9.7). In a statistical analysis of these data, Young *et al.* (1978) concluded that mercury in these seafood organisms from discharge areas was not concentrated significantly above levels measured in island and coastal control specimens.

Table 9.7. Mean concentrations (ppm ww) and standard deviations (or range) of mercury in edible (muscle) tissue of 15 seafood organisms from several outfall and reference sites in the Southern California Bight. From original data supporting Young et al., 1978 and Young et al., 1981. The number of samples from each site are shown in parentheses.

| COMMON NAME | POINT DUME | COASTAL SITES | | | | | ISLAND SITES | | |
		PALOS VERDES	SAN PEDRO BAY	LAGUNA BEACH	DANA POINT	SAN DIEGO	SANTA CATALINA	SAN CLEMENTE	CORTEZ BANK
Black abalone	--	0.011 ±0.004 (6)	--	--	0.010 ±0.002 (5)	--	0.006 ±0.004 (3)	0.023 ±0.025 (6)	--
Purple-hinge scallop	--	0.059 ±0.009 (3)	--	0.025 ±0.007 (3)	..	--	0.028 ±0.021 (2)	--	0.025 -- (1)
Red sea urchin	--	0.006 -- (3)	--	0.026 -- (5)	--	--	0.024 -- (3)	--	--
Yellow crab	--	--	0.079 ±0.087 (7)	--	0.103 ±0.059 (3)	--	--	--	--
California spiny lobster	0.283 ±0.010 (2)	--	--	0.305 ±0.098 (6)	--	0.092 -- (1)	0.277 ±0.096 (3)	--	--
Ridgeback prawn	--	--	0.039 ±0.007 (10)	--	0.052 0.025 (10)	--	--	--	--
Pacific sanddab	--	0.085 ±0.008 (4)	0.113 ±0.032 (10)	--	--	--	0.094 ±0.055 (3)	--	--
California halibut	--	0.283[2] ±0.064 (3)	--	--	--	0.222 ±0.031 (1)	--	--	--
White croaker	--	0.144 ±0.174 (3)	0.185 ±0.018 (3)	--	0.282 ±0.038 (3)	--	--	--	--

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Table 9.7. (continued)

COMMON NAME	POINT DUME	COASTAL SITES PALOS VERDES	SAN PEDRO BAY	LAGUNA BEACH	DANA POINT	SAN DIEGO	SANTA CATALINA	ISLAND SITES SAN CLEMENTE	CORTEZ BANK
California scorpionfish	--	0.439 ±0.251 (4)	--	--	0.817 ±0.656 (10)	--	0.284 ±0.091 (3)	--	--
Bocacio	--	0.187 - (1) 0.123 ±0.02 (2)	0.130 ±0.018 (3)	--	--	--	--	0.310 ±0.032 (3)	--
Kelp bass	--	045 (1.9-2.2) (4)	0.36 (0.12-1.1)	--	--	--	0.43 (0.077-0.50) (5)	--	--
Pacific bonito	--	0.370 (0.27-0.38) (3)	0.24 (0.12-0.45) (7)	--	--	--	--	--	--
Northern anchovy	--	0.077 (0.062-0.12) (10)	0.078 (0.03-0.12) (4)	--	--	--	0.067 (0.022-0.12) (10)	--	--
Market squid	--	0.078 (0.078-0.15) (3)	--	--	--	--	0.054 (10)	-- (0.031-0.078)	--

These data agree with an early study showing that mercury concentrations in fish were not increased by exposure to point sources or contaminated sediments. As shown in Figure 9.10, total mercury concentrations in composites of liver from replicate 1971-72 collections of Dover sole at 17 sites ranged fourfold from 0.071 ppm ww at a site at Santa Catalina Island to 0.300 ppm ww in comparable samples from Redondo Canyon in southern Santa Monica Bay (de Goeij et al., unpublished data). The range for the Santa Catalina collection was 0.071 to 0.160 ppm ww. Concentrations in fish taken from the highly contaminated Palos Verdes shelf were equally low, ranging from 0.089 at a site near San Pedro Canyon to 0.112 ppm ww at a site several km west of the outfall. The three highest concentrations were in the fish from Redondo Canyon and fish from deep water sites in Santa Monica Bay (0.24 ppm ww) and offshore of the San Pedro Canyon site (0.235 ppm ww). Later samples taken at Palos Verdes by Eganhouse et al. (1978) produced a mean of 0.124 ppm ww (range 0.05 to 0.236), similar to the concentrations reported by de Goeij and Guinn (1972a and b).

Data from the 1984 NOAA NS&T Benthic Surveillance Program are in general agreement with these observations. The lowest total liver mercury concentrations in hornyhead turbot were 0.084 ppm ww at San Pedro Canyon and 0.100 ppm ww at a nearshore Santa Monica Bay site. Slightly higher concentrations occurred in hornyhead turbot from Dana Point (0.104 ppm ww) and San Diego Bay (outside the harbor, 0.137 ppm ww; Figure 9.11). Liver mercury concentrations were clearly lower in white croaker from the Seal Beach site than from the Dana Point reference site, and lower in barred sand bass from San Diego Harbor compared to the Dana Point reference site.

Mercury concentrations in muscle of a white shark, in all spiny dogfish and mako sharks, and in some blue sharks, thresher sharks, California scorpionfish, swordfish, kelp bass, and pointer crabs (Muria guadichaudii) equaled or exceeded the historical FDA action limit of 0.5 ppm ww. Many other popular sportfish had concentrations within a factor of 5 of the limit (0.1 ppm ww). The current FDA action limit is 1.0 ppm ww. This was exceeded by kelp bass from Palos Verdes, some blue sharks and spiny dogfish, all mako sharks and swordfish, white shark, and some California scorpionfish from Dana Point (Table 9.6).

Organic mercury is the dominant form of mercury in muscle tissue of fish and macroinvertebrates from the Southern California Bight. In a study of several species at Palos Verdes, organic mercury accounted for an average of 70.8 percent of the total mercury in Dover sole, 87.1 percent in the pointer crab, and 70 percent in the ridgeback prawn (Eganhouse and Young, 1978)

SUMMARY AND CONCLUSIONS

Although inputs from sewage have declined during the past decade, other sources may have dominated, and continue to dominate, inputs of mercury to the Bight. These may include direct fallout and run-off, but no recent studies have attempted to document them as dominant sources. Submarine hot springs may also represent an important but unquantified source of mercury to this coastal ecosystem.

There have been, and continue to be, strong gradients in total mercury content of sediments along the Southern California Bight mainland shelf. Contaminated epicenters existed near the sewage discharges in Santa Monica Bay and at Palos Verdes and in scattered locations in Los Angeles-Long Beach harbors, at or near Marina del Rey, and in San Diego Harbor.

Despite inputs from sewage and abnormally high levels in sediments from some areas, local sources of mercury are generally not causing excess contamination in marine organisms. Mussels from Los Angeles-Long Beach harbors in 1982 indicated a gradient of increasing mercury contamination toward inner harbor sites such as the Dominquez Channel area. Elsewhere, it has been difficult to associate mercury contamination of mussels with proximity to known or presumed sources such as sewage outfalls. However, it is possible that mercury in fecal material of seals and sea lions is a source at some remote sites, thus obscuring large-scale gradients that might be attributable to direct anthropogenic sources. Measurements in other marine organisms along the coast do not show that inputs and contaminated sediments are sources to fish and macroinvertebrates. On the other hand, it is clear that the mercury that is present does undergo biomagnification and occurs in high concentrations (above the FDA limit) in large fish and sharks sampled near known point sources.
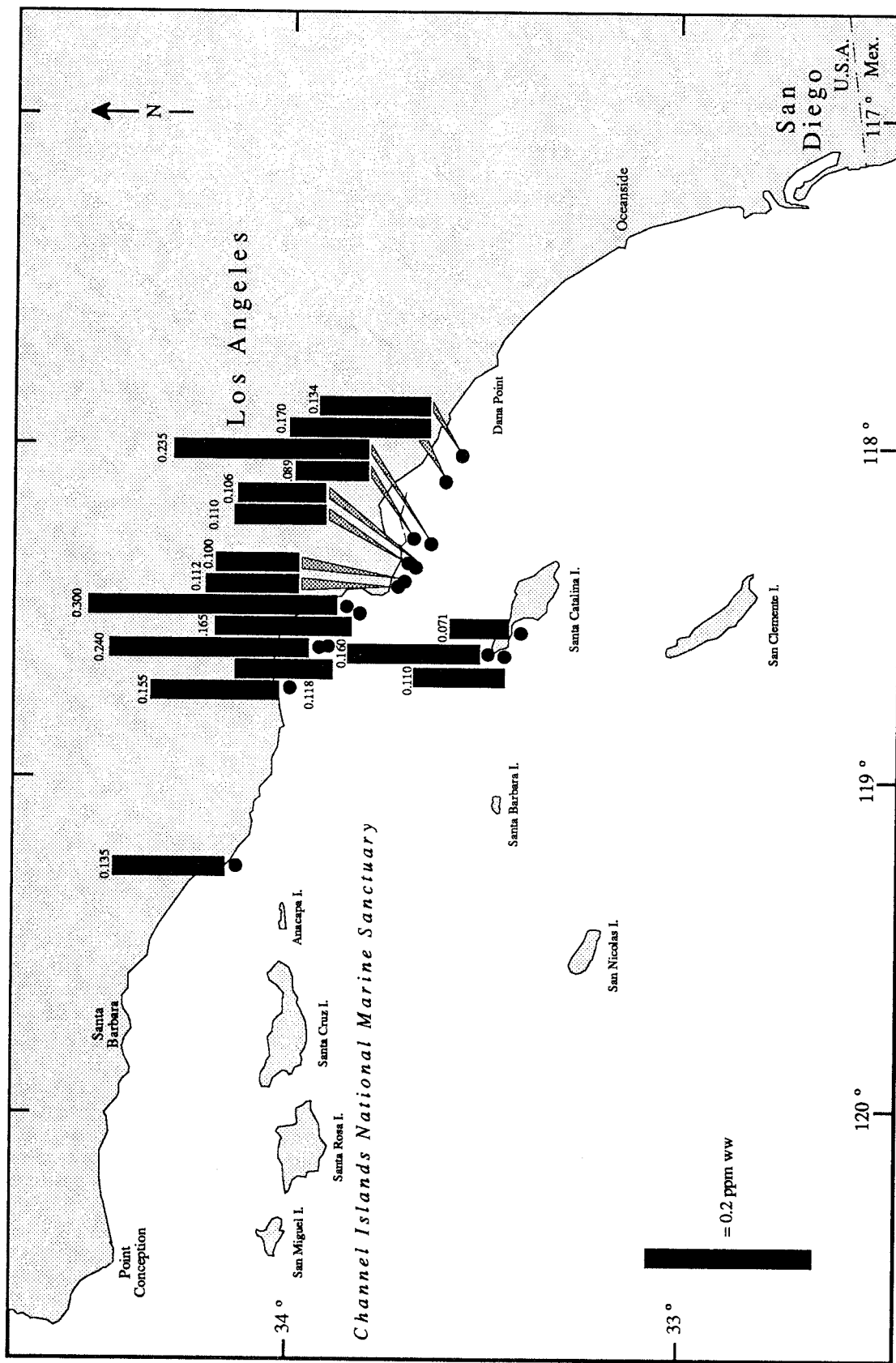
Figure 9.10. Mercury concentrations (ppm ww) in liver tissue of Dover sole collected in the Southern California Bight 1971-1972. Source: de Goeij et al. (unpublished).
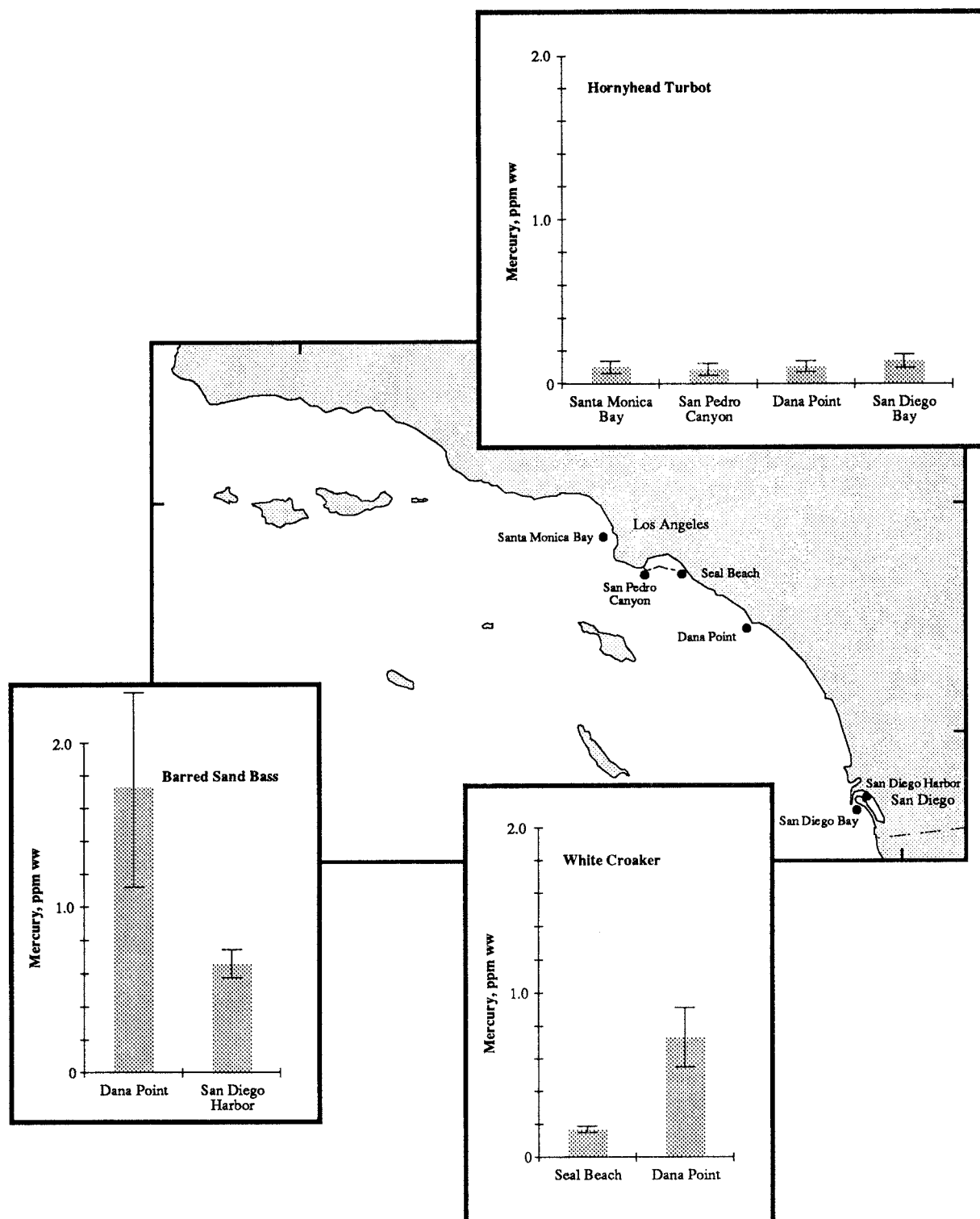
Figure 9.11. Concentrations of mercury measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

Long-term monitoring of mercury in mussels from three widely spaced sites suggests there has been a large-scale coherence of interannual variations that occurred irrespective of the decreasing inputs from sewage. It is possible mercury trends in Bight organisms are controlled by natural or large-scale anthropogenic events. However, the lack of data on mercury in biota from embayments, in sediments from most of the coastal shelf, and for input sources other than sewage including natural sources such as submerged hot springs, preclude a firm assessment and leave considerable uncertainty about anthropogenic sources and their control.

INFORMATION NEEDS

Mercury in sewage effluents has declined to concentrations at or near prevailing detection limits. As a consequence, mass emissions can now only be reported to one significant figure (for example, less than 1 mt per year; SCCWRP, 1988). To track further reductions, it will be necessary to reduce detection limits at least tenfold.

Mercury continues to be frequently monitored in sediments and biota in surveys around discharge sites. However, there is a growing paucity of comparable data from distant sites along the coastal shelf. Such data may be needed in the future to judge the effectiveness of both local and global management actions on regional levels. New measurements should be made from dated cores from deep basins in southern California to find out if concentrations, on a regional basis, have declined since they were last noted in 1969-71.

Spatial and temporal trends of mercury in sediments and stationary biota (mussels) from inner harbor areas need to be monitored. Such areas include the Domiguez Channel area of inner Los Angeles-Long Beach harbors and the Rhine Channel shipyard area of Newport Bay. Other areas with high vessel activity should also be more closely examined for trends in mercury.

Finally, it would be helpful to know to what extent natural events are in fact contributing to spatial and temporal variations of mercury in regional and specific localities (such as pinniped haul out sites). Attempts should be made to confirm the association of high mercury content in mussels and other shellfish with spatial and temporal trends in marine mammal concentrations. Likewise, if geothermal springs and upwelling of deep water are indeed important local and regional sources of mercury, surveys should be conducted to confirm those associations.

CHAPTER 10

SELENIUM

Selenium is a widely occurring natural element with a diverse set of agricultural and industrial uses. It has been used since the early 1900s in plant pesticides. Its widespread use has been curtailed because it is persistent in soil, contaminates food crops, is expensive, and is toxic to non-target organisms. Industrial uses include applications as components in production of glass, pigments, rubber, metal alloys, textiles, petroleum, medical therapeutics, and photo emulsion. A familiar domestic use is of an active ingredient in shampoos to control dandruff in humans and mange in dogs (Eisler, 1985).

Selenium is thought to be an essential biological element, although this role has not been conclusively and universally established. It has demonstrated anticarcinogenic properties and appears to protect against the toxic effects of other elements such as arsenic, cadmium, copper, mercury, silver, and thallium (Goyer, 1986; Menzer and Nelson, 1986). Selenium is a constituent of glutathione peroxidase, an enzyme that detoxifies organic contaminants, peroxides, and free radicals that can initiate carcinogenesis (Burau, 1985).

However, selenium is toxic at high concentrations as are nearly all trace elements. Acute exposure has been shown to result in central nervous system effects and liver and spleen damage (Goyer, 1986). Woock et al. (1987) demonstrated that elevated dietary concentrations of selenium caused teratogenesis and decreased larval survival in freshwater fish. The acute and chronic results of environmental selenium contamination became apparent in 1985. Delivery of Federal irrigation water was halted to 42,000 acres of agricultural land in the San Joaquin Valley because of acute selenium poisoning of fish and wildlife at the Kesterson Wildlife Refuge. Twelve evaporation ponds built to hold agricultural wastewater were found to concentrate selenium to highly toxic levels resulting in wildlife mortalities and deformities (Burau, 1985).

Acute toxicity of selenium appears to occur at relatively high concentrations when route of exposure is water. For example, the 48 hour LC_{50} concentration for larvae of the Pacific oyster has been reported to exceed 10 ppm (Glickstein, 1978), while the 96-hour LC_{50} value for larvae of winter flounder (*Pseudopleuronectes americanus*) was determined to be greater than 14 ppm (U.S. EPA, 1980).

It is, however, the chronic toxicity of selenium that represents the more significant environmental concern. Gross abnormalities observed in fish and waterfowl at the Kesterson Wildlife Refuge are one example of chronic effects. Other field and laboratory studies have shown that reproductive disorders, selective bioaccumulation, and growth retardation may result from longer term exposure to much lower concentrations than those causing acute toxicity (Eisler, 1985).

The biokinetics of selenium appear to exhibit a wide degree of variability, even among related species of bivalve mollusks. Fowler and Benayoun (1976b) found that mussels (*Mytilus galloprovincialis*) accumulated tetravalent selenium more than hexavalent selenium, and that smaller mussels sequestered relatively greater amounts than did larger specimens of the same species. Fowler and Benayoun (1976a) reported that the highest concentrations were found in soft body tissues other than gill, muscle, and mantle when the route of exposure was seawater. In specimens collected from the natural environment and presumed to be in equilibrium with ambient selenium concentrations, very different results were obtained. Mantle tissue accumulated the highest concentrations of the element. Fowler and Benayoun (1976a) suggested that the water route may be relatively unimportant in attaining equilibrium concentrations in tissue. Selenium is assimilated into zooplankton tissues, which may account for the long residence time of selenium in the ocean. This would also suggest that selenium is recycled in surface waters (Reinfelder and Fisher, 1991).

Micallef and Tyler (1987) studied toxicity interactions of mercury and selenium in *M. edulis* and found a complex relationship. While administration of selenium with mercury appeared to reduce mercury toxicity, the timing of the doses as well as the relative proportion of selenium to mercury affected the degree of protection. Pelletier (1986) obtained similarly complex results in a study of simultaneous bioaccumulation of inorganic and organic forms of selenium and mercury in *M. edulis*. Surprisingly, however, no toxic effects were observed when selenium was administered alone. Selenium exposure resulted in none of the adverse impacts observed in other species.

Weathering of naturally occurring materials accounts for most of the selenium mobilized into the environment. Some rocks (shale in particular) have been identified as being especially rich in selenium (Burau, 1985). In the United States, anthropogenic sources account for about 4600 mt of selenium inputs into the environment annually. Of this total, 33 percent originates from fossil fuel combustion, 59 percent from industrial processes, and 8 percent from municipal wastes (Eisler, 1985). Fowler and Benayoun (1976a) noted that anthropogenic sources, specifically fossil fuel combustion and agricultural and industrial uses, may be significant in the global selenium flux.

Selenium inputs to the Southern California Bight have been measured only for sewage. For the 14-year period 1974-87, inputs were measured only for sewage from the Hyperion Treatment plants and discharges of the CSDLAC and Point Loma (SCCWRP, 1987a and 1988). The emission from these sources ranged from 17.8 mt per year in 1974 to 7.0 mt per year in 1987 with a peak of 23.0 mt per year in both 1977 and 1978 (Figure 10.1). In general, inputs have been lower since 1979 (7.0 to 15.3 mt per year) than before (16.9 to 23.0 mt per year). Including data from CSDOC, the 1985 total emissions were 13.3 mt distributed as follows: Hyperion, 3.0; CSDLAC, 5.5; and CSDOC, 4.8 (SCCWRP, 1986).

Comparing selenium in sewage with that in agriculture return water may be of special interest in California. Annual average sewage concentrations in 1985 ranged from less than 5 parts per billion (ppb) in Hyperion sewage effluent to 11 ppb in CSDLAC effluent and to as high as 46 ppb in Hyperion sludge (SCCWRP, 1986). In previous years, such as 1977, concentrations were 10 ppb in Hyperion effluent, 16 ppb in CSDLAC effluent, and 1680 ppb in Hyperion sludge (Schafer, 1979). These waste stream concentrations are comparable to those in agriculture drain water (50 ppb) entering the reservoir of Kesterson National Wildlife Refuge where selenium is accumulated to levels causing deformities in fish and reproductive impairment in aquatic birds (Burau, 1985). However, in contrast to the situation at Kesterson, the selenium inputs by way of sewage into coastal waters of the Southern California Bight do not appear to lead to increased concentrations in fish or shellfish, even near the sources. On the contrary, as shown below, selenium concentrations are lower in marine life near the urban coastal discharge area than away from them. This leaves open the possibility of ocean discharge as an alternative for managing agriculture wastewater.
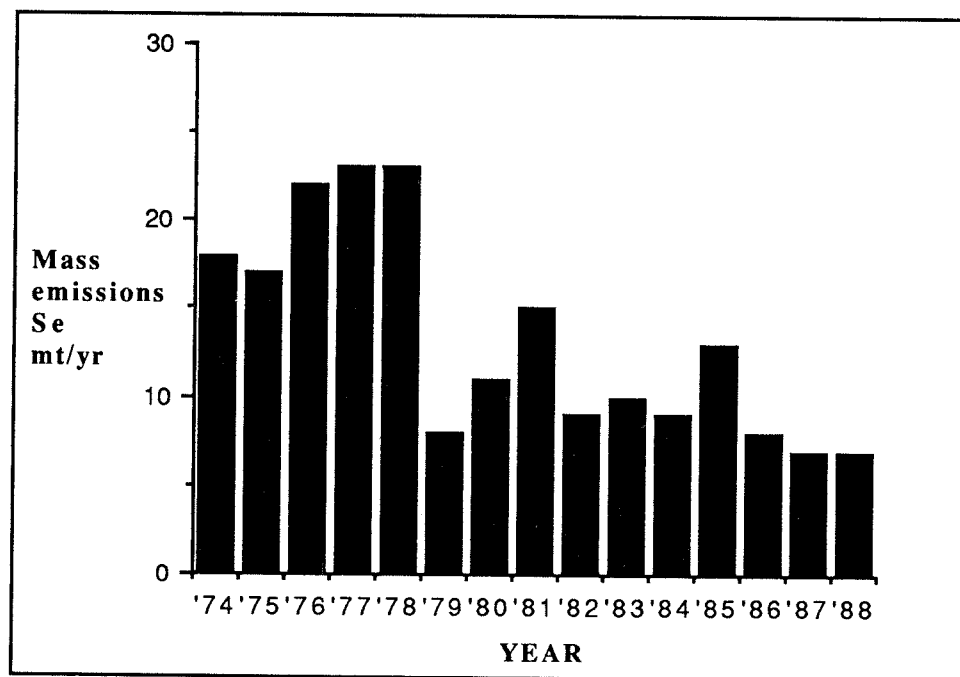

Figure 10.1. Combined annual mass emissions of selenium for seven southern California wastewater dischargers, 1974-88. Source: SCCWRP, 1989.

SELENIUM IN SEDIMENT

There is a major lack of data on concentrations of selenium in sediments from the Bight. Selenium measurements were not included in early regionwide trace element surveys such as those of Galloway (1972a and b) and SCCWRP (1973), or in other more recent shelf survey efforts including the SCCWRP 60-m Survey and 1985 reference survey (Thompson et al., 1987). Likewise, selenium was not measured in most bay and harbor trace element surveys at localities such as Marina del Rey (Soule and Oguri, 1987), Los Angeles-Long Beach harbors (Soule and Oguri, 1980a and b), Newport Bay (MBC and SCCWRP, 1980), or San Diego Harbor (Ladd et al., 1984)

According to Young (1974), background selenium concentrations at the bottom of cores from Palos Verdes were about 0.2 to 0.3 ppm dw. In a core collected in July 1971 northwest of the Whites Point (Palos Verdes) outfalls, the selenium concentration rose from 0.2 to 0.3 ppm dw at 30 cm, to 5.0 to 6.0 ppm dw at 10 cm, and then dropped slightly to 4.0 to 5.0 ppm dw at the surface. This surface concentration was similar to a median concentration of 6.5 ppm dw (range 4.0 to 14.3) reported for 5-cm surface sediment samples from nine stations along the 60-m isobath from a 1974 survey by CSDLAC (Stull and Baird, 1985). In addition, Stull and Baird's data suggest a major decline in sediment selenium to a 1980 median of 2.8 ppm dw (range 1.5 to 4.6; Figure 10.2). Selenium measurement was discontinued by CSDLAC after 1980.

Selenium was measured quarterly at many sites surrounding the Orange County deepwater outfall off Huntington Beach beginning July 1985. The mean concentration at 13 sites along the 60-m isobath was 1.0 ppm dw (range 0.024 to 3.6 ppm dw) during the 1985-86 survey and 0.72 ppm dw (range 0.26 to 4.4 ppm dw) during the 1986-87 survey period (CSDOC 1987; 1988).

Selenium was measured in sediment by the NOAA NS&T Program. Selenium levels in 1984 and 1985 were highest in sediments from Royal Palms (Palos Verdes). Low levels of selenium were detected in sediments from San Diego Bay, Dana Point, and Santa Monica Bay.
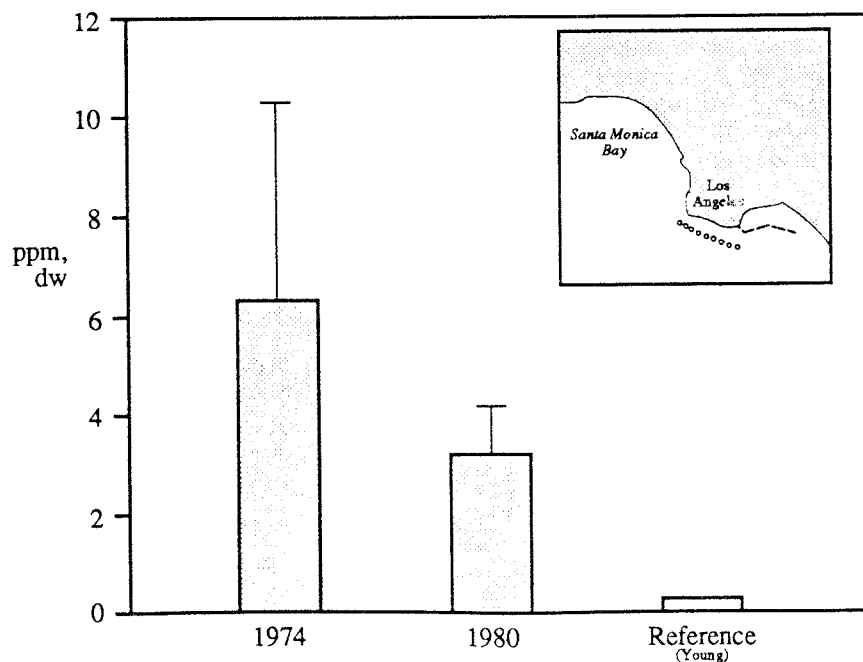

Figure 10.2. Mean selenium concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC (Stull and Baird, 1985). The reference value is based on a core sampled by Young (1974). Inset shows approximate locations of sites sampled by CSDLAC.

SELENIUM IN MUSSELS

Data on selenium concentrations in mussels of southern California are limited. The NS&T Mussel Watch Project is the only large-scale sampling effort among those reviewed for this discussion that analyzed tissue concentrations of selenium on a consistent basis. The data do not show any notable trends with respect to proximity to municipal outfalls, species differences, or general site characteristics (Figure 10.3). Ranges of mean values were relatively narrow, from 2.44 to 4.57 ppm dw in *M. californianus* and 2.03 to 4.77 ppm in *M. edulis*. The maximum concentrations for these species were found at Point Conception and Marina del Rey, respectively.

The 1971 SCCWRP study, the 1974 SCCWRP harbors study, and the EPA Mussel Watch Program did not analyze samples for selenium. CMW performed seven analyses at six sites in 1982 with concentrations ranging from 0.8 to 0.9 ppm dw at two sites in Los Angeles-Long Beach harbors (*M. edulis*), to 1.7 ppm dw at Royal Palms (Palos Verdes), 2.4 to 2.6 ppm dw at Oceanside, and 2.0 to 2.5 ppm dw at Point Loma (*M. californianus* at the latter three sites).

Among three embayments, the 1986 NOAA NS&T Mussel Watch data indicate that comparable selenium concentrations occurred at two Santa Monica Bay sites (Point Dume, 3.63 ppm dw and Marina del Rey, 4.77 ppm dw) and one San Diego Bay site (3.2 ppm dw). However, a slightly lower mean concentration occurred in samples from the third area, the Los Angeles-Long Beach breakwater (2.5 ppm dw). This breakwater concentration is higher than levels reported by CMW of 0.8 and 0.9 ppm dw for two nearby inner Los Angeles-Long Beach harbors sites sampled in 1982. This may indicate that there are significant analytical differences between the two programs.

Overall mean levels of selenium measured nationwide by NOAA's NS&T Program between 1986 and 1989 were similar for *M. edulis* and *M. californianus*. The mean level of selenium in *M. edulis* was 2.471 ppm dw (median, 2.267 ppm dw) and for *M. californianus* the mean was 2.936 ppm dw (median, 2.833 ppm dw). The range of site mean values was greatest for *M. edulis* (from below detection limits to 7.75 ppm dw).

There are no data sufficient for documenting long-term trends in selenium in mussels of the Southern California Bight. Bodega Head, in the northern part of the state, was the only site in California subject to time-series measurements. Between August 1981 and August 1986 selenium concentrations in *M. californianus* increased from 1.8 to 3.1 ppm dw (Phillips, 1988). NOAA's NS&T Program has documented no significant changes in selenium concentrations in mussels sampled annually since 1986 (NOAA, 1989).

Together, the NOAA NS&T and CMW data suggest either that there are no selenium contamination epicenters in the Bight or that there is selenium depletion in mussels near the major urban areas.
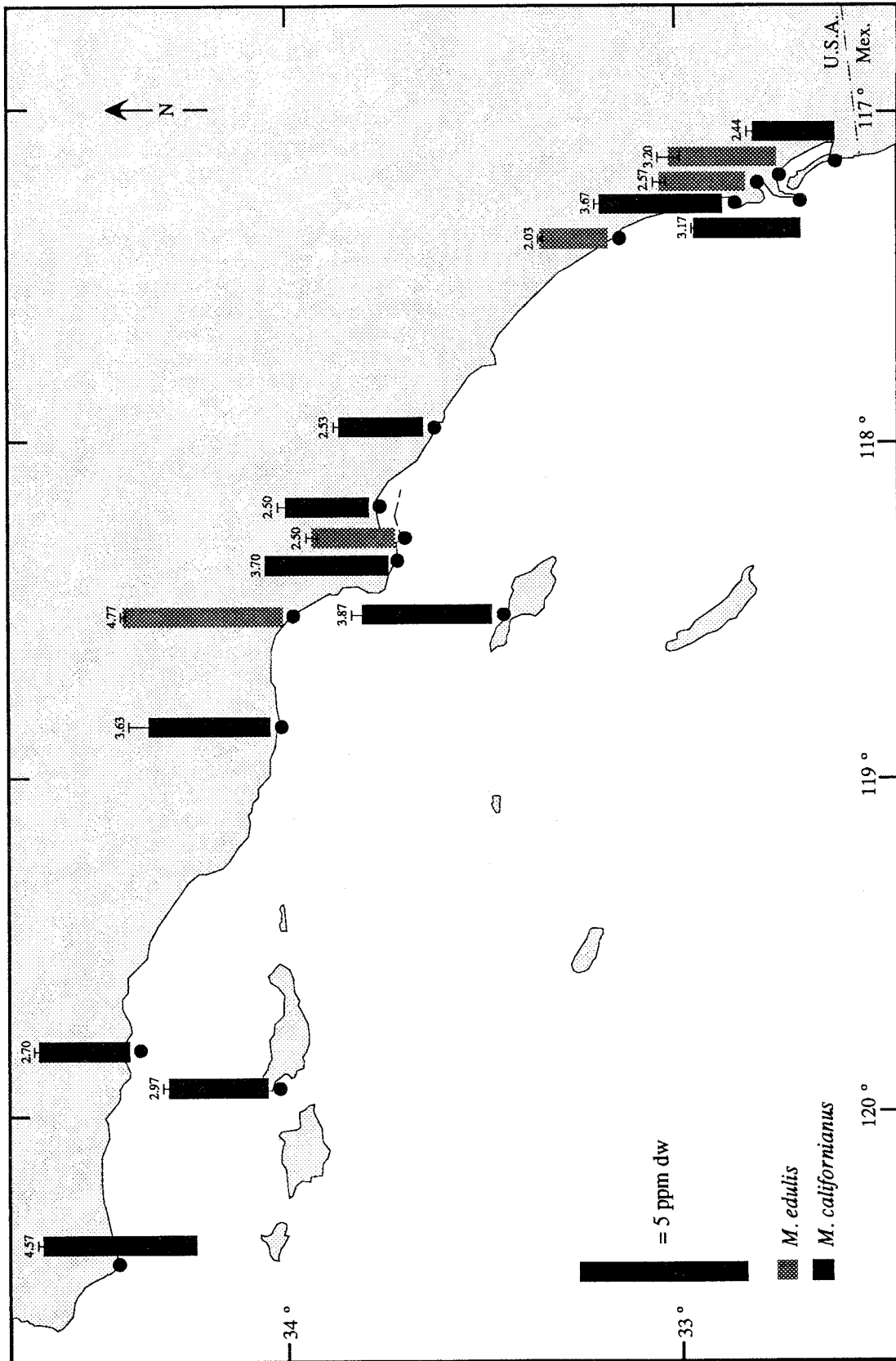
Figure 10.3. Selenium in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

10-5

SELENIUM IN FISH AND OTHER SPECIES

Selenium has been measured in at least 300 samples of 39 species of marine organisms from the Bight. These include 21 species of fish, 2 sharks, 3 echinoderms, 3 crustaceans, and 5 mollusks (Table 10.1). The principal data sets examined included a 1971-72 survey of livers of Dover sole (de Goeij et al., 1974); surveys of edible tissues of seafood organisms collected from several bay, harbor, and coastal ecosystems collected between 1975 and 1980 (Goeders, 1982); the 1984 NOAA Benthic Surveillance data (NOAA, 1987a); a survey of Dover sole and crab from the early 1970s by Fowler et al. (1975); and data from 1984-85 monitoring surveys of the CSDOC (1985).

Selenium concentrations in various tissues of fish and macroinvertebrates were generally around 1.0 ppm ww (Table 10.1). The highest concentrations in non-hepatic tissues were 15.7 ppm ww in muscle from Dover sole from off Santa Barbara (Fowler et al., 1975), 7.9 ppm ww in mantle tissue from a composite of market squid from Santa Catalina Island (Goeders, 1982; Schafer et al., 1982), 4.1 ppm ww in whole tissue of tellinid clams from near the Orange County outfalls (CSDOC, 1986), and 3.9 ppm ww in muscle of yellow crabs from Dana Point (Goeders, 1982). Liver tissue concentrations ranged from 0.29 ppm ww in hornyhead turbot from San Pedro Canyon near Palos Verdes, to 12.8 ppm ww in white croaker from near Seal Beach (NOAA, 1988).

In general, selenium concentrations in muscle of pelagic, demersal, and bay or estuarine fish were similar. Concentrations in pelagic fish ranged from means of 0.26 to 0.66 ppm ww in northern anchovy to 1.28 to 2.52 ppm ww in Pacific bonito. Sharks were similar to pelagic fish with concentrations in individual specimens ranging from 0.22 to 0.78 ppm ww (Table 10.1). Despite evidence to the contrary from other studies, Goeders (1982) concluded that selenium does not undergo biomagnification in most food webs. However, she found evidence that selenium does undergo biomagnification in a food web of Newport Bay with an accumulation factor of 1.46, a value similar to the increase in marine fish of the Salton Sea, a saline lake in the southern California desert (Goeders, 1982).

Selenium was measured in popular seafood organisms in three studies. The most extensive was a 1975-77 collection of nine popular seafood species from six coastal and island sites sampled as part of a regional seafood study (Young et al., 1978; Goeders, 1982). These data (Table 10.2) show that in four of nine species (purple-hinge scallop, red sea urchin, yellow crab, and California spiny lobster) selenium was lower in collections from the Palos Verdes (Whites Point) discharge area than at one or more distant reference sites (Table 10.2). Selenium concentrations were higher at Palos Verdes than at reference sites for muscle of three species: black abalone, kelp bass, and bocaccio (Table 10.2). Two species (Pacific sanddab and California halibut) had comparable concentrations at Palos Verdes and island reference sites. Fowler et al. (1975) reported slightly lower muscle selenium concentrations in yellow crab and Dover sole from Palos Verdes (mean, 5.14 and 0.27 ppm ww, respectively) than from a site off Santa Barbara (15.66 and 0.38 ppm ww, respectively).

Levels of selenium in livers of marine fish from the Southern California Bight ranged from 0.36 to 8.44 ppm ww. Selenium in composites of livers of Dover sole collected in 1971 and 1972 ranged from 0.40 ppm ww at a site off Huntington Beach to 1.70 at a site near the west end of Santa Catalina Island (de Goeij and Guinn, 1972a, b). There was no obvious increase of selenium in livers of fish from outfall areas such as Palos Verdes but rather some evidence of depressed values in these fish (de Goeij et al., 1974). As shown in Figure 10.4, selenium concentration on the mainland shelf ranged from 0.4 to 1.45; whereas, at the offshore Santa Catalina Island sites they ranged from 1.05 to 1.70 ppm ww.

Selenium in Dover sole was not measured in the 1984 or 1985 NOAA NS&T surveys, but data are available for selenium in liver from a related species, hornyhead turbot (Figure 10.5). Mean concentrations in liver of hornyhead turbot ranged from 0.36 and 0.49 ppm in San Diego Bay and at San Pedro Canyon (off Palos Verdes)to 2.38 and 2.39 ppm ww, respectively in Santa Monica Bay and at Dana Point. Selenium concentrations were much higher in two other species, with comparable levels for white croaker from Seal Beach (8.44 ppm ww) and Dana Point (8.43 ppm ww) but slightly higher values for barred sand bass from San Diego Harbor (8.38 ppm ww) than from Dana Point (6.15 ppm ww). Concentrations of 3.2 and 6.1 ppm ww were reported in livers of two samples of striped mullet sampled from the Tijuana Estuary in April 1984 (Agee, 1986). It is noteworthy that selenium concentrations in livers of these marine fish are in the same range as concentrations in California freshwater fish (0.5 to 9.1 ppm ww; Agee, 1986)

Table 10.1. Selenium concentrations (ppm ww) in edible tissues of marine organisms of the Southern California Bight.

Common Name	Site	Date	No. of Samples	Mean	Median	Min	Max	Standard Deviation	Source
Zooplankton (whole)	Point Dume/ Santa Monica Bay	1981	4	0.395	0.345	0.240	0.650	0.185	Goeders, 1982
Zooplankton (whole)	Santa Catalina Island	1981	1	0.820	-	.		-	Goeders, 1982
Enteromorpha (whole)	Newport Bay	1978	3	0.613	0.580	0.470	0.790	0.163	Goeders, 1982
Green Algae	Newport Bay	1978	1	0.580	-	-	-	-	Goeders, 1982
Kelp (internal stipe)	Los Angeles Harbor	1979	5	0.276	0.260	0.050	0.480	0.164	Goeders, 1982
Gaper clam (neck)	Cabrillo Beach/LA Harbor	1979	5	0.434	0.540	0.010	0.700	0.290	Goeders, 1982
Clam (tellina) (whole soft)	Orange County outfall	1985	3	1.730	<1.2	<1.00	4.100	2.000	CSDOC, 1985
Purple-hinge scallop (muscle)	Palos Verdes - KOU Towers	1976	7	0.414	0.370	0.160	0.620	0.164	Goeders, 1982
Purple-hinge scallop (muscle)	Laguna	1975	3	0.613	0.600	0.570	0.670	0.051	Goeders, 1982
Purple-hinge scallop (muscle)	Santa Catalina Island	1975	3	0.733	0.330	0.180	1.640	0.792	Goeders, 1982
Black abalone (muscle)	San Clemente Island	1975	5	0.234	0.200	0.070	0.440	0.136	Goeders, 1982
Black abalone (muscle)	Palos Verdes - Whites Point	1976	2	0.485	0.485	0.420	0.550	0.092	Goeders, 1982
Market squid (mantle)	Santa Catalina Island	1979/80	5	2.156	0.860	0.290	7.900	3.225	Goeders, 1982
Ridgeback prawn	Palos Verdes	1980	4	0.870	0.560	0.350	1.880	0.696	Goeders, 1982
Ridgeback prawn	Orange County outfall	1985	7	0.070	All samples: less than detection level (0.220)				CSDOC, 1985
California spiny lobster	Palos Verdes - Royal Palms	1976	4	0.443	0.440	0.310	0.580	0.111	Goeders, 1982
California spiny lobster	San Diego area	1977	2	0.525	0.525	0.400	0.650	0.177	Goeders, 1982
California spiny lobster	Santa Catalina Island	1976	3	1.510	1.430	1.150	1.950	0.406	Goeders, 1982
Yellow crab	Palos Verdes	1976	3	1.413	1.770	0.880	1.770	0.514	Goeders, 1982
Yellow crab	Dana Point	1976	2	3.040	3.040	2.930	3.900	0.156	Goeders, 1982
Yellow crab	Palos Verdes-Point Vicente	1974	14	5.140	-			-	Fowler et al 1975
Yellow crab	Santa Barbara	1974	14	15.660	-			-	Fowler et al 1975
Sea star (pyloric caeca)	Orange County outfall	1985	2	-	-	<.07	<.072	-	CSDOC, 1985
Green sea urchin (gonad)	Orange County outfall	1985	1	<.12	-	-	-	-	CSDOC, 1985
Red sea urchin (gonad)	Palos Verdes Whites Point	1976	3	0.380	0.490	0.160	0.490	0.190	Goeders, 1982
Red sea urchin (gonad)	Corona del Mar	1975	2	0.800	0.800	0.760	0.830	0.050	Goeders, 1982
Red sea urchin (gonad)	Santa Catalina Island	1975/76	4	0.560	0.610	0.390	0.690	0.160	Goeders, 1982
Striped mullet, adult	Newport Bay	1978	3	0.653	0.780	0.380	0.800	0.240	Goeders, 1982
Striped mullet, juvenile	Newport Bay	1978	3	0.667	0.740	0.380	0.880	0.260	Goeders, 1982
Topsmelt	Newport Bay	1978	3	0.907	0.880	0.540	1.300	0.380	Goeders, 1982
White croaker	Los Angeles Harbor	1979	5	0.558	0.530	0.420	0.730	0.138	Goeders, 1982
	Orange County outfall	1985	1	0.058	-	-	-	-	CSDOC, 1985
Yellowfin croaker	Newport Bay	1978	3	0.783	0.780	0.780	0.790	0.010	Goeders, 1982
California halibut	Los Angeles Harbor	1979	4	0.522	0.480	0.250	0.880	0.280	Goeders, 1982
California halibut	Palos Verdes	1976	4	0.458	0.415	0.140	0.860	0.342	Goeders, 1982
California halibut	San Diego area	1976	2	0.480	0.480	0.390	0.570	0.127	Goeders, 1982
California tonguefish	Orange County outfall	1985	6	0.107	0.097	0.080	0.170	0.032	CSDOC, 1985
Dover sole	Palos Verdes-Point Vicente	1974	11	0.270	-	-	-	-	Fowler et al 1975
Dover sole	Santa Barbara	1974	12	0.380	-	-	-	-	Fowler et al 1975
Hornyhead turbot	Orange County outfall	1985	3	0.114	0.122	0.093	0.130	0.019	CSDOC, 1985
Pacific sanddab	Palos Verdes	1975/76	4	0.740	0.775	0.470	0.940	0.199	Goeders, 1982
Pacific sanddab	Santa Catalina Island	1973	3	0.693	0.730	0.560	0.790	0.119	Goeders, 1982
Speckled sanddab	Orange County outfall	1985	4	0.093	<.120	<.090	0.220	0.016	CSDOC, 1985
Bocaccio	San Clemente Island		3	0.120	0.040	0.030	0.290	0.147	Goeders, 1982
Bocaccio	Palos Verdes		1	0.600	-	-	-	-	Goeders, 1982
Bocaccio	Palos Verdes		3	0.356	0.245	0.260	0.560	0.178	Goeders, 1982

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Table 10.1. (continued)

| Common Name	Site	Date	No. of Samples	Mean	Median	Min	Max	Standard Deviation	Source
Striped bass	Newport Bay		3	1.133	1.370	0.610	1.420	0.450	Goeders, 1982
Spotted sand bass	Newport Bay		3	1.343	1.390	1.220	1.420	0.110	Goeders, 1982
Barred sand bass	Orange County outfall		3	0.081	0.074	0.069	0.100	0.017	CSDOC, 1985
Kelp bass	Palos Verdes		4	1.060	0.094	0.245	2.120	0.780	Goeders, 1982
Kelp bass	Santa Catalina Island		5	0.810	0.760	0.410	1.340	0.034	Goeders, 1982
Scorpionfish	Palos Verdes		4	0.658	0.465	0.440	1.260	0.402	Goeders, 1982
Jack mackerel	San Pedro Channel		2	1.125	1.125	0.870	1.380	0.361	Goeders, 1982
Jack mackerel	Santa Catalina Island		1	1.340	-	-	-	-	Goeders, 1982
Jack mackerel	Santa Monica Bay		1	1.520	-	-	-	-	Goeders, 1982
Jack mackerel	Newport		1	0.640	-	-	-	-	Goeders, 1982
Northern anchovy	LA harbor Bait Barge		5	0.348	0.410	0.210	0.139	0.231	Goeders, 1982
Northern anchovy	Port Hueneme		1	0.260	-	-	-	-	Goeders, 1982
Northern anchovy	Oxnard		1	0.440	-	-	-	-	Goeders, 1982
Northern anchovy	Huntington Beach		3	0.663	0.520	0.430	1.040	3.290	Goeders, 1982
Pacific bonito	Redondo		1	1.280	-	-	-	-	Goeders, 1982
Pacific bonito	Huntington/Newport		2	2.520	2.520	1.030	4.010	2.107	Goeders, 1982
Pacific mackerel	Orange County outfall		2	0.041	-	<.075	0.047	-	CSDOC, 1985
Pacific mackerel	San Pedro Channel		4	0.540	0.505	0.410	0.740	0.161	Goeders, 1982
Pacific mackerel	Santa Catalina Island		1	0.740	-	-	-	-	Goeders, 1982
Pacific sardine	Point Dume		2	0.780	0.780	0.560	1.000	0.311	Goeders, 1982
Mako shark	Santa Catalina Island		1	0.390	-			-	Goeders, 1982
Mako shark	San Pedro		1	0.220	-			-	Goeders, 1982
Mako shark	Newport		3	0.680	0.700	0.560	0.780	0.111	Goeders, 1982
White shark	Santa Catalina Island		1	0.453	0.370	0.330	0.660	0.180	Goeders, 1982
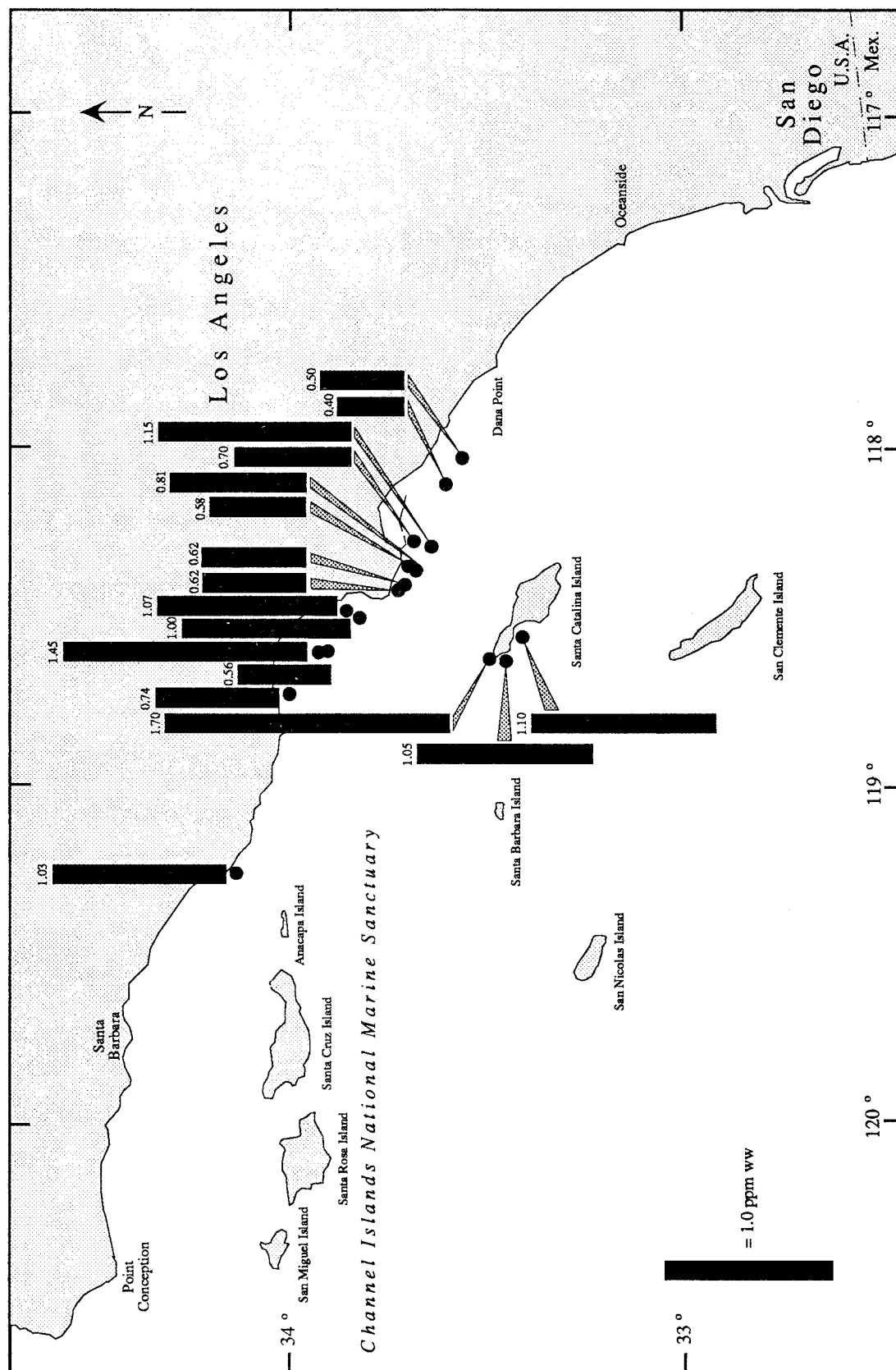
Figure 10.4. Selenium concentrations (ppm ww) in liver tissue of Dover sole collected in the Southern California Bight in 1971-1972. Source: de Goeij et al. (unpub).
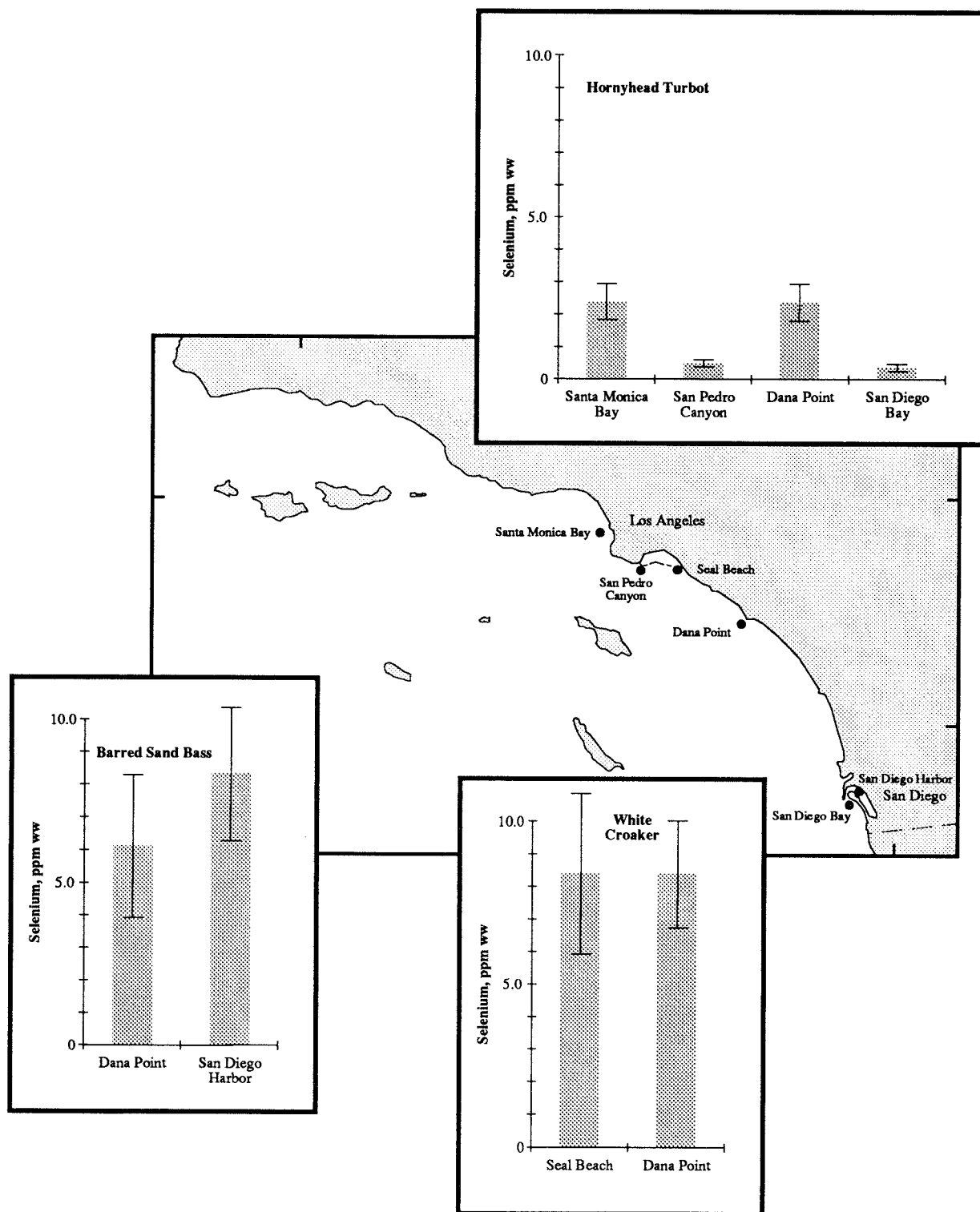
Figure 10.5. Concentrations of selenium measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

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Table 10.2 Selenium (ppm ww) in edible tissue of nine popular seafood organisms collected 1975-78 from six southern California coastal and island sites. Number of samples is given in parentheses. Source: Goeders 1982; Young and Mearns 1982.

COMMON NAME	COASTAL SITES				ISLAND SITES	
	PALOS VERDES	LAGUNA BEACH	DANA POINT	SAN DIEGO	SANTA CATALINA	SAN CLEMENTE
black abalone [1]	0.49 (2)					0.23 (5)
purple-hinge scallop [2]	0.41 (7)	0.61 (3)			0.73 (3)	
red sea urchin [3]	0.38 (3)	0.48 (1)			0.43 (4)	
yellow crab [4]	1.41 (3)		3.04 (2)			
California spiny lobster [4]	0.46 (4)			0.53 (2)	1.51 (3)	
Pacific sanddab [4]	0.74 (9)				0.69 (3)	
California halibut [4]	0.46 (4)				0.48 (2)	
kelp bass [4]	1.06 (5)				0.81 (5)	
bocaccio [4]	0.34 (3)					0.12 (3)

[1] foot
[2] whole soft tissue
[3] gonad
[4] muscle

There are no seafood criteria for selenium in the United States. Nauen (1983) identified several international criteria including 0.3 ppm ww for Chile (all food stuffs) and 1.0 ppm ww for fish and fish products in Australia (except for three states where the limit is 2.0 ppm ww). The Chilean standard was exceeded by most organisms from the Southern California Bight and the Australian standards were exceeded by squid, lobster, crab, bass, jack mackerel, and Pacific bonito from a variety of sites.

SUMMARY AND CONCLUSIONS

Existing data are just sufficient to suggest that elevated selenium concentrations have occurred in sediments at Palos Verdes. No other areas of enhancement are evident in the limited data base. Like arsenic (chapter 4) there is no clear-cut gradient of selenium concentration in marine organisms suggesting severe

contamination from urban sources. For most species surveyed, including mussels, macroinvertebrates, and fish, there is either no evidence of increases near Palos Verdes or the Los Angeles-Long Beach harbors areas. The only exceptions were slightly higher concentrations (by a factor of 2 to 3) in black abalone, kelp bass, and bocaccio from Palos Verdes relative to reference sites. Since these species have not been re-sampled since 1977, it is impossible to determine if concentrations have declined commensurate with levels in offshore sediments or sewage.

There may be evidence of selenium deficiency in fish associated with urban areas. Selenium deficiency may itself be cause for concern. As noted above, selenium is required for production of the enzyme glutathione that mediates detoxification of other contaminants. NOAA-sponsored studies by Brown *et al.* (1987) indicate that glutathione activity in marine organisms from the Palos Verdes area is incapacitated by binding with metabolites of DDT and PCBs. To compensate for reductions in glutathione caused by exposure to DDT and PCBs, organisms from the Palos Verdes area could be using available selenium to produce glutathione peroxidase. Thus, selenium depression might be a result of chlorinated hydrocarbon contamination of these organisms. Recovery from pollution may result in increasing selenium concentration over time in some marine life from Palos Verdes and adjacent areas.

INFORMATION NEEDS

Due to the severe inconsistency of species, sites, and tissues sampled among data sets, it is not possible to judge if selenium concentrations have been changing over time in marine life of the Bight. Similarly, the lack of selenium measurements in dated cores precludes an assessment of regional trends in selenium in sediment. Dated cores should be measured to help determine long-term, regionwide terms.

The selenium data reviewed for this report may have bearing on evaluating alternatives for the disposal or treatment of selenium-contaminated agriculture wastewater in California. One alternative is ocean disposal. The selenium data reviewed here for southern California indicate that emissions into the open coastal zone about 5 to 15 mt selenium per year have resulted in local accumulations of selenium in marine sediments near one outfall, but no accumulation in the bottom-dwelling organisms (such as flatfish) intimately associated with those contaminated sediments. Thus, it is not necessarily the case that discharge of selenium to the ocean will result in bioaccumulation. In any case, the importance of finding an alternative to protect inland wildlife may justify additional research and monitoring near existing coastal discharges.

Judging by the degree to which southern California seafood organisms exceed selenium quality criteria for two nations (Chile and Australia), it seems important to determine what safe levels really are for consumers of seafood from the Southern California Bight. This should be done even though, like arsenic, selenium may not be from anthropogenic sources.

CHAPTER 11

SILVER

Silver is a familiar metal that has played an important role in human history through its uses in commerce and industry. Today, the principal application of silver is associated with photography and the manufacturing of film and photographic plates. Electronics, jewelry, coins, flatware, and medical applications represent other major uses.

Silver is not normally found in animal tissue. When exposure occurs, silver is usually sequestered in tissue as silver sulfide. Although large acute doses have caused death in higher experimental animals, chronic exposures manifest themselves in a variety of less severe ways in many tissues (Goyer, 1986). However, Chapman (1978) listed silver as one of the three most toxic metals (with cadmium and mercury) in the aquatic environment; and Eisler (1981) identified silver as one of the most toxic metals to mollusks. Silver is incorporated into zooplankton tissues and may be recycled in oceanic surface waters for long time periods (Reinfelder and Fisher, 1991).

Calabrese et al. (1984) studied the effects of long-term silver exposure on growth, metal accumulation, and histopathology of M. edulis. In comparison to effects of copper evaluated in the same study, those of silver were less severe. For example, significant amounts of silver were accumulated only at the highest test concentration (10 µg/L). No growth inhibition was noted at the highest test concentration. Similar to results obtained for other animal species (including humans) silver appeared to be deposited in membrane and connective tissues of various organs. George et al. (1986) found that in common with other metals such as cadmium, copper, and mercury, silver can induce the synthesis of metal-binding proteins resembling metallothionein in M. edulis.

Discharges from sewage treatment plants represent an important source of silver into the marine environment. In the Southern California Bight, an estimated 27 mt were discharged from eight treatment plants in 1985 (SCCWRP, 1987a). One outfall in particular, the Hyperion Plant outfall in Santa Monica Bay, accounted for over half of the silver in the sewage total (SCCWRP, 1987a). By contrast, only 0.3 mt were discharged into the Bight from the Los Angeles River in 1985 (Schafer and Gossett, 1988). However, other source routes have not been investigated. Stephenson et al. (1979a and b) noted a correlation of silver "hot spots" (regions where elevated concentrations of silver are found in mussel tissue) with urban areas, and suggested that silver may be among the best trace element indicators of anthropogenic inputs such as large ocean outfalls near urban industrial areas.

Silver may also be the only monitored contaminant that has not decreased substantially in wastewater during the past two decades. Indeed, based on data collected by SCCWRP (1987a; 1988), silver mass emissions may have increased from 20 to 25 mt per year in the mid-1970s to 27 to 30 mt per year in the 1980s (with a peak of 42.2 mt in 1979) but decreased to 22 mt in 1986 and 15 mt in 1987 (Figure 11.1).
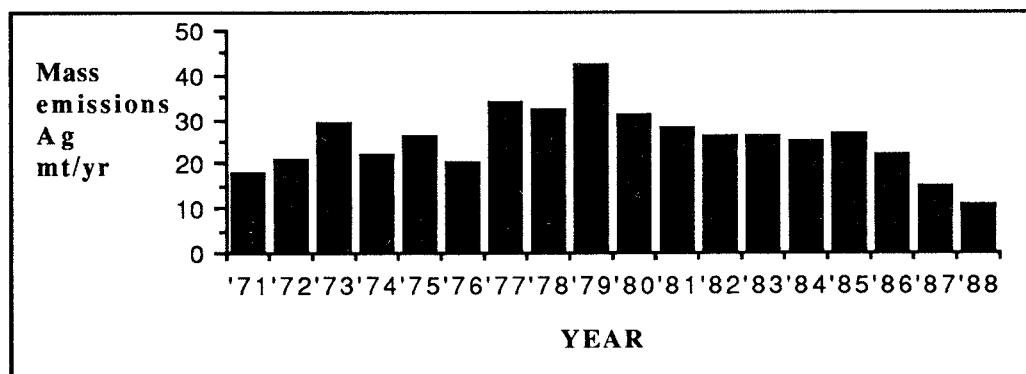

Figure 11.1. Combined annual mass emissions of silver for seven southern California wastewater dischargers, 1971-88. Source: SCCWRP, 1989.

Silver radioisotopes have been historical contaminants in the Southern California Bight. The artificial silver nuclides [108] Ag and [110] Ag from nuclear bomb testing in 1962 appeared in albacore collected from off San Diego in 1964 that may have traced 2-year movement of water masses from the central Pacific to the Southern California Bight (Folsom *et al.*, 1970).

SILVER IN SEDIMENT

Silver concentrations in surface sediments of the Southern California Bight measured in selected surveys from 1970 to 1985 spanned three orders of magnitude, from 0.01 ppm dw measured in 1985 near Port Hueneme to 18 ppm dw measured on the Palos Verdes shelf in 1977 (Table 11.1). There have been very strong local gradients of silver in sediments with the highest concentrations near sewage outfalls. For the rural coastal shelf region, the range for sediment silver was 0.01 to 0.88 ppm dw; in bays and harbors, 0.27 to 4.0 ppm dw; and near outfalls, 0.08 to 18 ppm dw. Medians ranged from 0.01 to 0.36 in shelf areas, 0.5 to 1.8 in bays and harbors, and 0.21 to 8.1 near outfalls.

For outfall areas, the Palos Verdes shelf and Santa Monica Bay areas showed consistently elevated median values. In fact, the seven medians for these two regions were the seven highest among the 25 reported in Table 11.1. Similarly, the five lowest median silver concentrations reported in the Bight occurred among the six values for the rural coastal shelf region.

Silver was measured in sediments at over 70 sites along the 60-m isobath in a 1977 synoptic survey (Word and Mearns, 1979). Concentrations ranged from 0.04 ppm dw at a site on the Santa Barbara shelf to 18.0 ppm dw at a Palos Verdes site (Table 11.1). From north to south, concentrations increased from a mean of 0.19 ppm dw on the Santa Barbara shelf to the means of 3.18 in Santa Monica Bay and 6.49 along the Palos Verdes shelf then decreased to a mean of 0.45 ppm dw off Orange County and remained low to the south except for a small increase (to a mean of 0.75) at Point Loma.

Concentrations were significantly lower at 13 remote coastal control sites re-sampled in 1985 (Thompson *et al.*, 1987). However, 1985 concentrations were comparable or only slightly lower at several outfall sites (Palos Verdes, Orange County, and Point Loma; Table 11.1).

The source of the nearly tenfold difference in silver concentration at the 13 reference sites sampled in 1977 and 1985 is probably due to differences in extraction and analysis methods. Silver is relatively easy to extract and measure using flame ionization atomic absorbtion spectrometry (AAS) in samples containing greater than about 1 ppm dw. Such high concentrations have prevailed in Santa Monica Bay and at Palos Verdes. However, at concentrations substantially below 1 ppm dw, which are common over most of the coastal shelf, flame ionization AAS is insensitive with the gram-quantity sample size commonly used for trace element extraction and analysis. Accordingly, carbon rod AAS was used to estimate silver concentrations in many samples taken by SCCWRP in regionwide surveys during the period 1977 to 1982 (such as Word and Mearns, 1979; Hershelman *et al.*, 1981; 1982). This is not a standard method. However, the values in the range of 0.01 to 0.10 ppm dw from non-outfall areas may be background levels.

Accepting all sediment silver values reported by SCCWRP for surveys taken between 1977 and 1982, an additional important statement can be made about silver distributions on the southern California shelf. Like other trace elements, silver concentrations in sediments from the relatively uncontaminated shelf between Point Dume and Port Hueneme increased significantly with depth (range 14 to 714 m) organic content (as measured by total volatile solids, range 0.8 to 6.8%) and percent silt (% <63μ) and decreased with percent solids. Analysis of the Hershelman *et al.* (1982) data indicates that concentrations increased from a mean of 0.11 ppm dw at 14 to 32 m, 0.16 ppm dw at 45 to 62 m, 0.23 ppm dw at 93 to 106 m, 0.33 ppm dw at 260 to 354 m, 0.43 ppm dw at 477 to 598 m, and then decreased slightly to 0.24 ppm dw at 713 to 745 m indicating that background concentrations are depth dependent (Hershelman *et al.*, 1982).

Table 11.1. Mean, median, minimum, and maximum silver concentrations in surface sediment from selected surveys, 1970-1985 in ppm dw.

Site	Year	N	Mean	Median	Minimum	Maximum	Standard Deviation	Source
Rural Coastal Shelf (60 meters only):								
Santa Barbara shelf	1977	11	0.19	0.10	0.04	0.88	0.25	1
	1985	4	0.01	0.01	0.01	0.01	0.002	2
Port Hueneme to Point Dume	1977	4	0.40	0.36	0.05	0.84	0.33	1
	1980	11	0.16	0.13	0.08	0.31	0.07	3
	1985	2	0.05		0.01	0.10	0.07	2
Newport to Dana Point	1977	3	0.2	0.21	0.11	0.27	0.08	1
	1978	6	0.13	0.08	0.05	0.40	0.14	4
	1985	1	0.01					2
Outfall Areas:								
Oxnard shelf	1971[a]	3	1.57	1.6	1.2	1.9	0.31	9
Santa Monica Bay	1970[a]	24	3.14	2.95	1.2	7.6	1.55	9
	1977[b]	13	3.18	2.2	0.98	8.9	2.53	1
	1978[b]	31	5.02	4.7	0.46	14	2.99	4
Palos Verdes shelf	1970[a]	22	2.68	2.8	0.55	5.7	1.35	9
	1977[b]	8	6.49	4.50	0.1	18	6.53	1
	1978[b]	8	7.69	8.10	2.30	12	3.32	4
	1985[b]	10	1.91	2.04	0.35	3.40	0.95	5
Orange County shelf	1970[a]	13	1.8	1.8	1.5	2.5	0.3	9
	1977[b]	11	0.45	0.45	0.24	1.1	0.24	1
	1978[b]	12	0.26	0.21	0.08	0.56	0.17	4
	1985[b]	9	0.52	0.45	0.32	0.87	0.18	7
Point Loma shelf	1970[a]	5	1.2	0.88	0.57	2.4	0.74	9
	1977[b]	6	0.75	0.79	0.37	0.96	0.21	1
	1985[b]	8	1.06	0.90	0.70	1.70	0.38	8
Bays and Harbors:								
Los Angeles-Long Beach harbors [a]	1978	11	0.7	0.5	0.5	1.6	0.4	10
Upper Newport Bay[a]	1980	8	0.49	0.51	0.27	0.63	0.13	11
Newport Bay	1974	11	0.78	0.90	0.6	1.2	0.35	13
San Diego Harbor[a]	1983	20	1.7	1.8	0.5	4.0	0.9	12
OVERALL		274			0.01	18		

a - all depths; b - 60-m only

1 Word and Mearns, 1979	5 Hyperion Treatment Plant, original data	9 SCCWRP, 1973; Galloway, 1972a and b
2 Thompson et al., 1987	6 CSDLAC, original data	10 Soule and Oguri, 1980a
3. Hershelman et al., 1982	7 CSDOC, original data	11 MBC and SCCWRP, 1980
4 Hershelman et al., 1981	8 City of San Diego, original data	12 Ladd et al.,1984
		13 Young et al., 1975

Surficial sediment silver measurements made by NOAA's NS&T Program (Figure 11.2) showed geographic trends and concentrations comparable to the SCCWRP 1977 data. Concentrations in southern California sediments (six sites) ranged from 0.51 to 1.27 ppm dw in 1984 and 0.09 to 0.89 in 1985. In 1984, the lowest mean concentration occurred at the Santa Monica Bay site and the highest at the Seal Beach site. In 1985, the lowest mean level was found outside San Diego Bay and the highest inside San Diego Bay. The overall mean silver concentration for all sites sampled by the NS&T Program between 1984 and 1989 was 0.45 ppm dw (median, 0.126 ppm dw). Site mean concentrations ranged from below detection limits to 6.30 ppm dw).
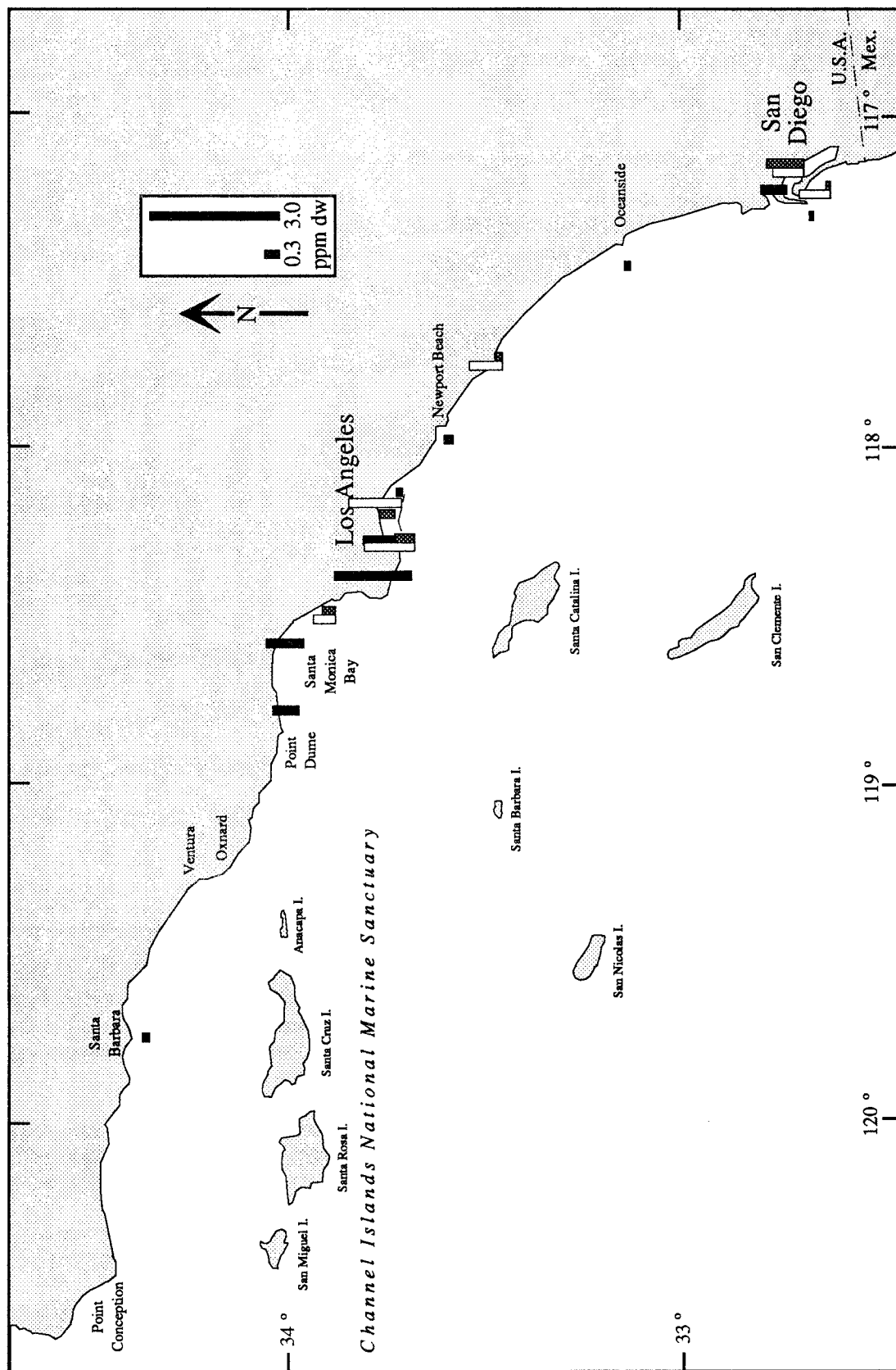
Figure 11.2. Silver concentrations in the surficial sediments of the Southern California Bight Based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 ( ) and 1985 ( ) and Mussel Watch Project for 1986 ( ) (NOAA, 1988 and NOAA, unpublished data).

In the NS&T Mussel Watch Project, southern California sediment concentrations of silver showed a consistent geographic distribution in 1986 and 1987, but were generally higher in 1987. Site means ranged from 0.12 to 1.8 ppm in 1986 and 0.22 to 3.7 ppm dw in 1987 (Figure 11.2). The site rankings with respect to sediment silver remained nearly identical. Maximum mean concentrations occurred at Royal Palms, Los Angeles-Long Beach harbors, and Marina del Rey. Minimum mean concentrations occurred at Point Loma, Oceanside, and Anaheim Bay (near Long Beach).

Despite the dominant silver input from sewage discharges, Katz and Kaplan (1981) concluded that the regionwide distribution in sediments of the Bight was not controlled by this source. This appears to be in sharp contrast to the opposite conclusion arrived at in the next section based on results for silver in mussels. Sediment surveys are considerably fewer for silver than for other trace metals. Notably lacking are data for marinas and recent data from most harbors.

Long and Morgan (1990) evaluated available data from sediment associated biological effects studies. They calculated a probable effects range (ER-L to ER-M) of 1.0 to 2.2 ppm for silver in sediment. Median sediment concentration exceeded the lower of these values at Santa Monica Bay and Palos Verdes. Median concentrations in bays and harbors did not exceed the lower concentration except in San Diego Harbor. Individual sites within Newport Bay however, have also exceeded the lower value. The ER-M value was only exceeded at Santa Monica Bay and Palos Verdes.

There no data sets suitable for judging the direction and magnitude of long-term trends of silver concentrations in sediments in recent years. However, very long-term trends are available for nearly a century preceding the early 1970s from dated cores analyzed by Bruland et al. (1974). In the San Pedro Basin, near Palos Verdes, silver concentrations were about 1.5 to 1.6 ppm dw through the 1940s then nearly doubled to 2.8 ppm dw in 1960 increasing to 3.4 ppm dw about 1970. A similar trend occurred in the Santa Monica Basin (1.1 in 1940 to 3.0 ppm dw in 1970) and was slightly detectable in the Santa Barbara Basin (1.1 in 1940 to 1.5 ppm dw in the late 1960s); but, no such increase was observed in the Soledad Basin 700 km to the south off Cabo San Lazaro in southern Baja California (all values about 2 ppm dw; Bruland et al., 1974) More recent core surveys (Finney and Huh, 1989; Schmidt and Reimers, 1987) did not include silver.

In summary, silver concentration have been highest in sediments near sewage outfalls. Sediments from San Diego Harbor have also contained elevated levels of silver. It is not known whether sediment concentrations have declined in recent years.

SILVER IN MUSSELS

Five large-scale surveys were found that can illustrate geographic trends in silver concentrations in mussels. Lowest concentrations of silver were found in mussels from Los Angeles-Long Beach harbors and Newport Bay (0.02 ppm dw) in 1982. The highest concentration of silver found in mussels was detected at Royal Palms on the Palos Verdes Peninsula in 1980 (64 ppm dw).

SCCWRP measured silver concentrations in digestive gland tissue of M. californianus collected at 17 sites in the Southern California Bight in 1971. Measured levels in the mussel tissue ranged from 0.3 ppm dw to 46 ppm dw (Figure 11.3). The distribution of concentrations suggests a positive correlation with proximity to urban centers in the Bight, and particularly to the Los Angeles area. In this context, the low value obtained at the Seal Beach site (0.3 ppm) would appear to be anomalous.

Not surprisingly, the CMW Program embodies the greatest number of results for concentrations of silver in southern California mussels. Grouped results for silver in M. californianus from CMW from 1977-86 show a range spanning three orders of magnitude, from 0.02 to 64 ppm dw. The results suggest two broadly defined areas in the Southern California Bight where resident mussels show elevated concentrations of silver: the region adjacent to Los Angeles and Santa Monica and the Point Loma region outside San Diego. Table 11.2 lists CMW sites with the 20 highest concentrations of silver. It is notable that all 20 are located within these two general areas.
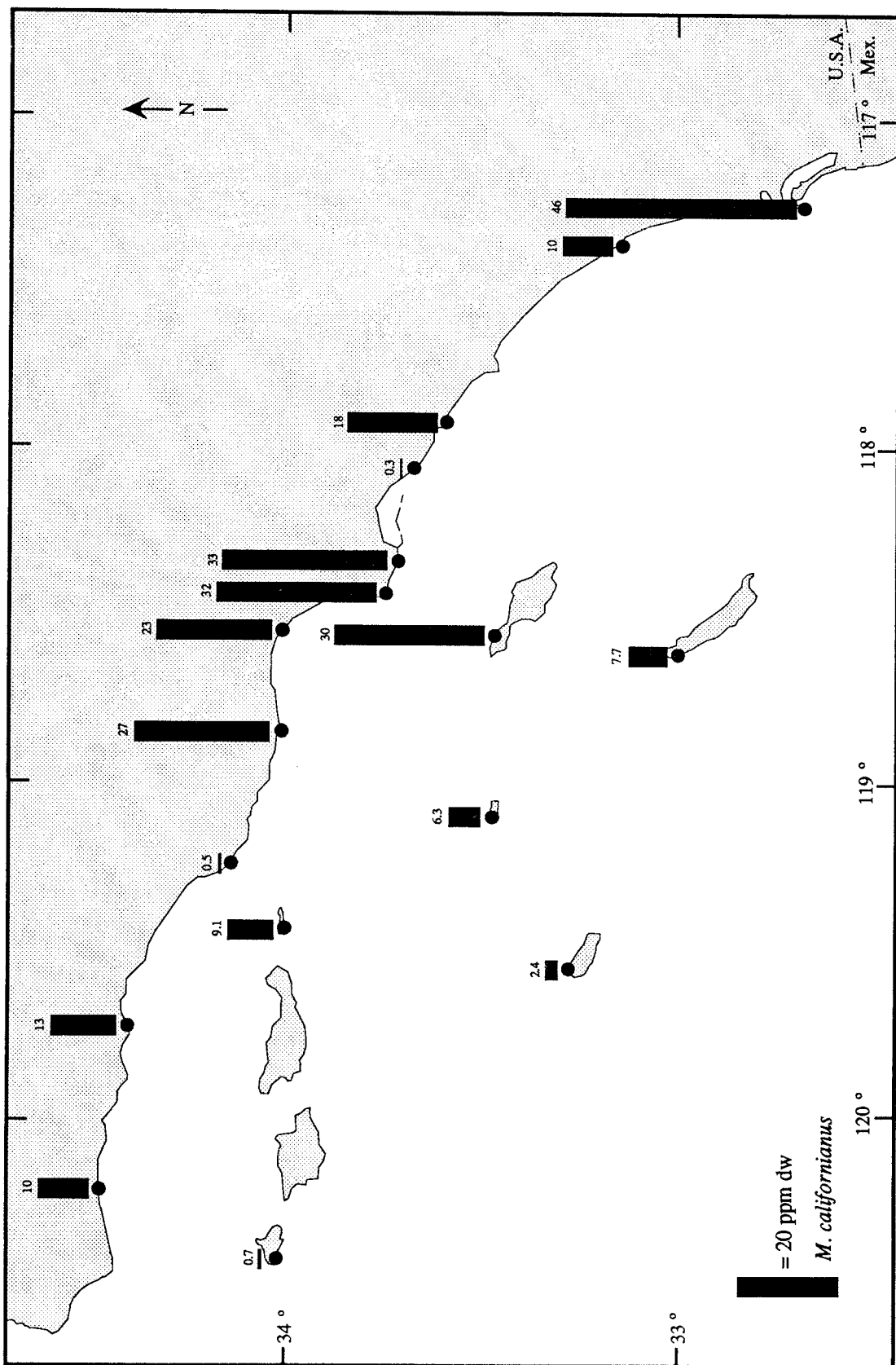
Figure 11.3. Silver in digestive gland of mussels sampled in 1971. Values shown are means of six samples, each sample equals one individual. Source: Young, 1974.

Table 11.2. Highest silver concentrations in southern California *M. californianus* tissue measured in CMW, 1977 through 1985 (Phillips, 1988).

Site	General Area	Date	Concentration (ppm dw)	Overall Rank
Royal Palms State Park	Los Angeles	12/80	64	1
NOSC Dolphin Tanks	Point Loma	12/80	58.8	2
Royal Palms State Park	Los Angeles	11/79	42.3	3
Palos Verdes	Los Angeles	12/80	42	4
Pink House	Point Loma	2/81	36.1	5
Point Vicente (Palos Verdes)	Los Angeles	12/80	34	6
El Segundo (Santa Monica Bay)	Los Angeles	12/80	29	7
Manhattan Beach (Santa Monica Bay)	Los Angeles	12/80	29	8
Redondo Beach (Santa Monica Bay)	Los Angeles	12/80	29	9
NOSC Dolphin Tanks	Point Loma	1/82	28.8	10
Playa del Rey (Santa Monica Bay)	Los Angeles	12/80	28	11
Point Vicente (Palos Verdes)	Los Angeles	11/79	27.7	12
Hermosa Beach (Santa Monica Bay)	Los Angeles	12/80	26	13
Sunset Cliffs	Point Loma	12/85	25.5	14
Pink House	Point Loma	1/82	25.1	15
Big Rock Beach (Santa Monica Bay)	Los Angeles	12/80	21	16
Malibu (Point Dume)	Los Angeles	12/80	20	17
Treatment Plant	Point Loma	12/85	16.9	18
Coast Guard Base	Point Loma	12/85	16.9	19
Bird Rock	Point Loma	11/79	14	20

There are apparently large differences in the ability of *M. edulis* and *M. californianus* to accumulate silver in their tissues. Of 164 CMW samples of silver concentrations in resident mussel tissue measured between 1977 and 1985 in the Southern California Bight, 123 were from *M. californianus* and 41 were from *M. edulis*. If these results are ranked from high to low by silver concentration, a distinct pattern of distribution by species emerges. That is, the 89 highest concentrations of silver from the CMW data set for resident mussels occur in *M. californianus*; of the next 42 ranked concentrations, 33 occur in *M. californianus* and 9 in *M. edulis*; and of the final 33 ranked concentrations, 32 are *M. edulis*. This is portrayed in a slightly different fashion in Figure 11.4.
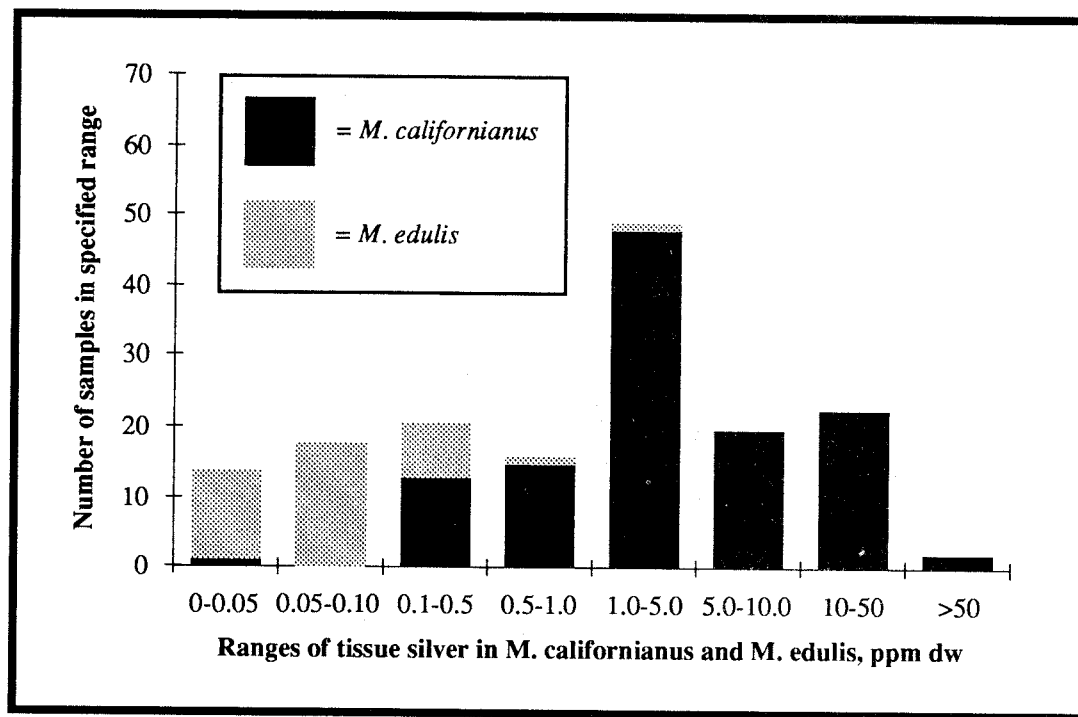
Figure 11.4. Distribution of sample measurements for silver by species of resident southern California mussels. Source: Phillips, 1988.

Based on these data, it would appear that *M. californianus* tends to sequester silver to higher levels than *M. edulis*. However, these results may result from environmental conditions at collection sites as well as from inherent species uptake characteristics, and could simply reflect the habitat preferences of the two mussel species (*M. californianus* prefers exposed open waters, while *M. edulis* is commonly found in more sheltered embayments). Direct comparison of concentrations measured in mussels of both species collected at a site where they co-occur is an obvious way to test whether significant species differences exist; however, this has not been explicitly pursued. Only one direct comparison of silver body burdens in resident mussels of both species collected from the same site is apparent from CMW data. In that occurrence, the concentration of silver in *M. californianus* exceeded that in *M. edulis* by greater than an order of magnitude (1.07 ppm versus 0.04 ppm at Newport Bay, 1980). While this is but one data pair, it is consistent with the apparent dominance of *M. californianus* in the ranking exercise.

There is some evidence of a large-scale geographic trend in silver concentrations in mussels. A combined CMW and Mexican Mussel Watch survey (Martin *et al.*, 1988) indicates that the southern California coastal background concentration of about 1.0 ppm dw in *M. californianus* is at least an order of magnitude above concentrations in samples from north central Baja California and northern California north of Point Reyes (about 0.05 to 0.1 ppm dw; Figure 11.5). If these latter concentrations represent "clean" background levels, then silver in mussels is abnormally high along nearly 100 km of California coastline, with epicenters in the Los Angeles and San Diego areas. Elevations above these background conditions occurred near the Crescent City outfall in northern California, in San Francisco and Monterey bays, the Los Angeles coast, and the Point Loma area of San Diego (Figure 11.5)

Near Los Angeles and Santa Monica, the proximity of major municipal outfalls combined with the northward local trend of the subsurface currents provides a possible explanation for the high mussel silver concentrations north of the Palos Verdes Peninsula. Outfalls at Whites point and in Santa Monica Bay contributed 77 percent of the total mass emission of silver to the Southern California Bight (SCCWRP, 1987a).
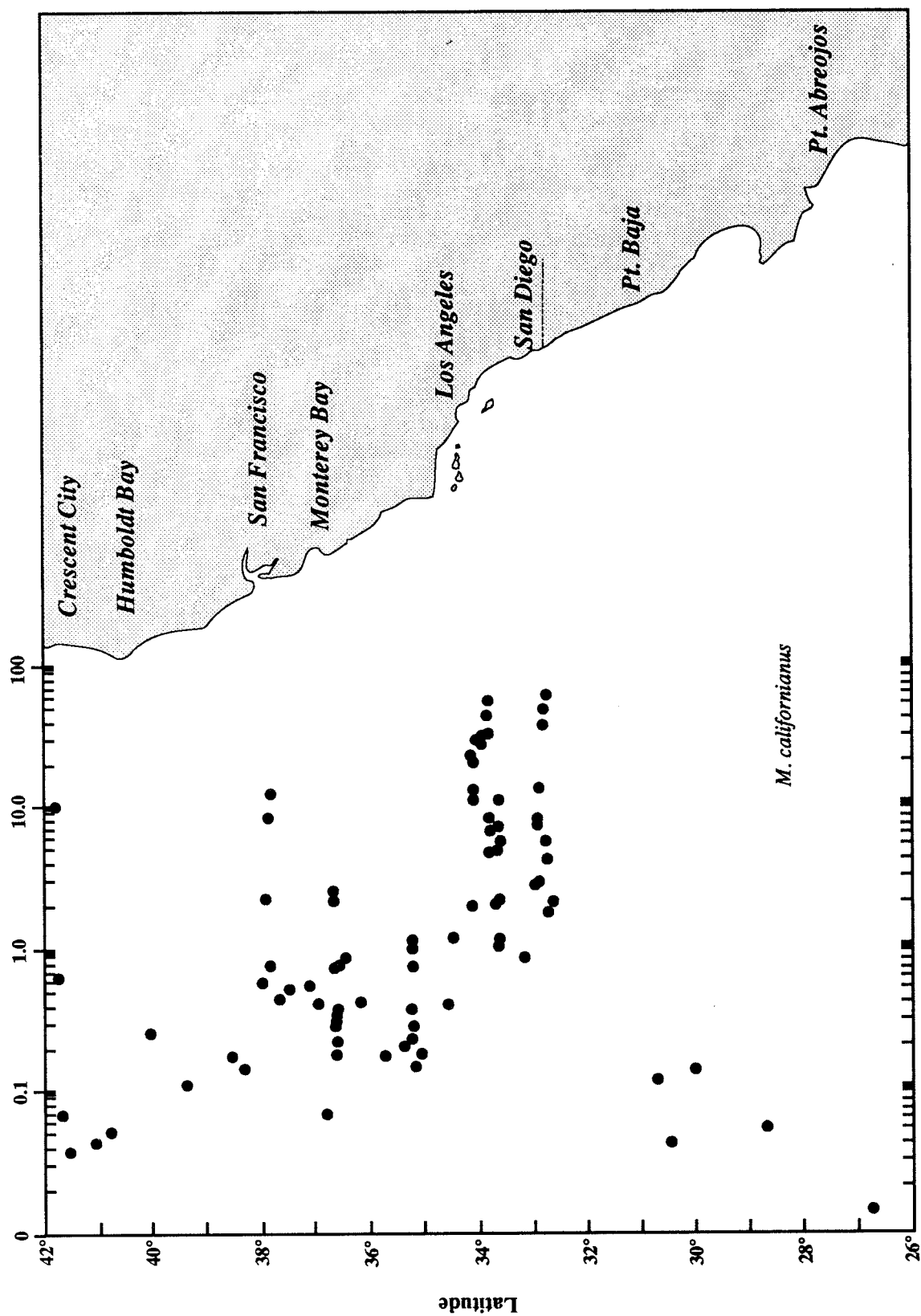
Figure 11.5. Concentrations of silver measured in resident mussels (ppm dw) 1977 through 1983. Note log scale. Source: Ladd et al., 1984.

11-9

The second area of high silver concentrations, near San Diego, is not as readily explained. The Point Loma treatment plant may account for a portion of the elevation in levels found in *M. californianus* tissue in that general locality, but Hayes and Phillips (1987) stated that the silver levels measured from this area are among the highest measured in the California program. They suggested that other inputs such as additional point source discharges, within San Diego Bay, or naturally occurring geological sources may contribute as well. The San Diego Region of the California State Water Resources Control Board (CSWRCB) may conduct a study to investigate the Point Loma area concentrations.

EPA Mussel Watch, which sampled seven sites in the Southern California Bight between 1976 and 1978, appears to show unusual short-term changes in body burdens of silver in *M. californianus* collected at three coastal sites in the southern portion of that region (Figure 11.6). Between 1976 and 1977, concentrations of tissue silver at Santa Catalina, Oceanside, and Point La Jolla increased 875 percent, 140 percent, and 379 percent, respectively. Concentrations at all three sites dropped back below 1976 levels in 1978. Reported mass emissions from the three major outfall systems in this area (JWPCP, Orange County, and Point Loma) do not indicate a corresponding point source explanation for these levels as total silver loadings from 1976 , 1977, and 1978 totaled 10.0, 8.9, and 13.7 mt, respectively (SCCWRP, 1987a).

The NS&T Program's Mussel Watch Project showed a smaller range of mean values for 16 sites located in southern California (Figure 11.7) than did the EPA Mussel Watch Program, spanning an order of magnitude versus two orders of magnitude in the latter effort. Highest concentrations were noted in *M. californianus* sampled at open coastal sites such as Point Dume, Point La Jolla, Royal Palms, Newport jetty, and Point Loma. Again, municipal discharges may account for some of these silver levels, but those at Point Dume and Newport suggest other sources are important as well.

Two surveys provide information to illustrate levels of silver in mussels from bays and harbors. Results from the CMW Program in Santa Monica Bay ranged over two orders of magnitude, from 0.2 ppm in *M. edulis* to 42 ppm in *M. californianus*. Among the various regions sampled by CMW using *M. californianus* (Table 11.3), Santa Monica Bay yielded the highest silver concentrations (1980 mean 24.8 ppm dw, range 11.0 to 42.0 ppm dw). This was over 3 times higher than the mean (7.74) from the entire southern California *M. californianus* collection (123 samples, 1977-85) which produced a range of 0.04 to 64.0 ppm dw. It was also over 25 times higher than silver in Santa Catalina Island *M. californianus* (mean 0.82, range 0.19 to 2.52 ppm dw; Table 11.3). In contrast, the 1986 NOAA NS&T Mussel Watch collection at Point Dume averaged only 1.83 ppm dw, considerably lower than the 1980 CMW samples (11.0 ppm dw) from this area.
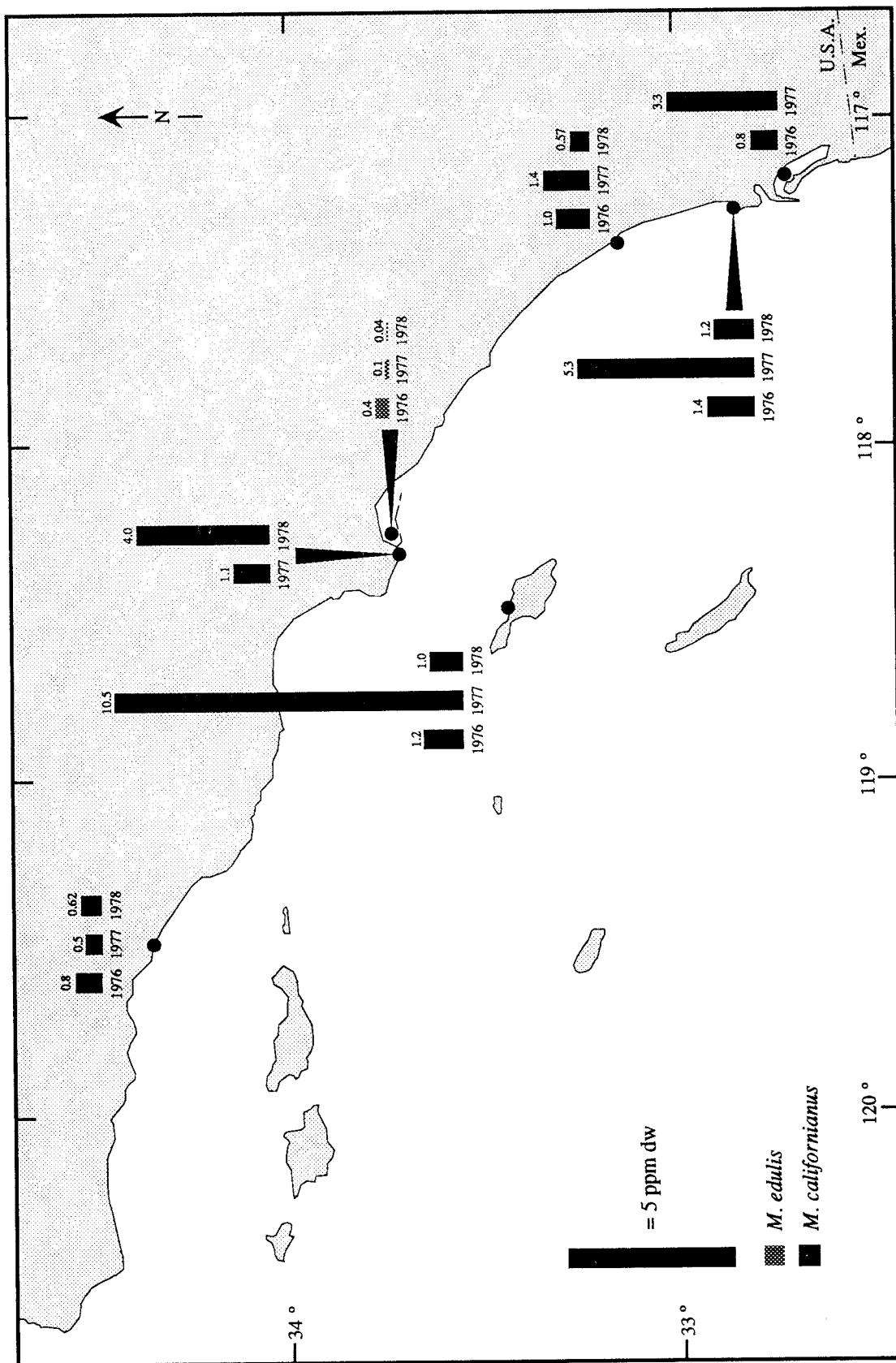
Figure 11.6. Silver in whole soft body tissue of mussels sampled in the Southern California Bight 1976 through 1978. Source: EPA Mussel Watch Program.
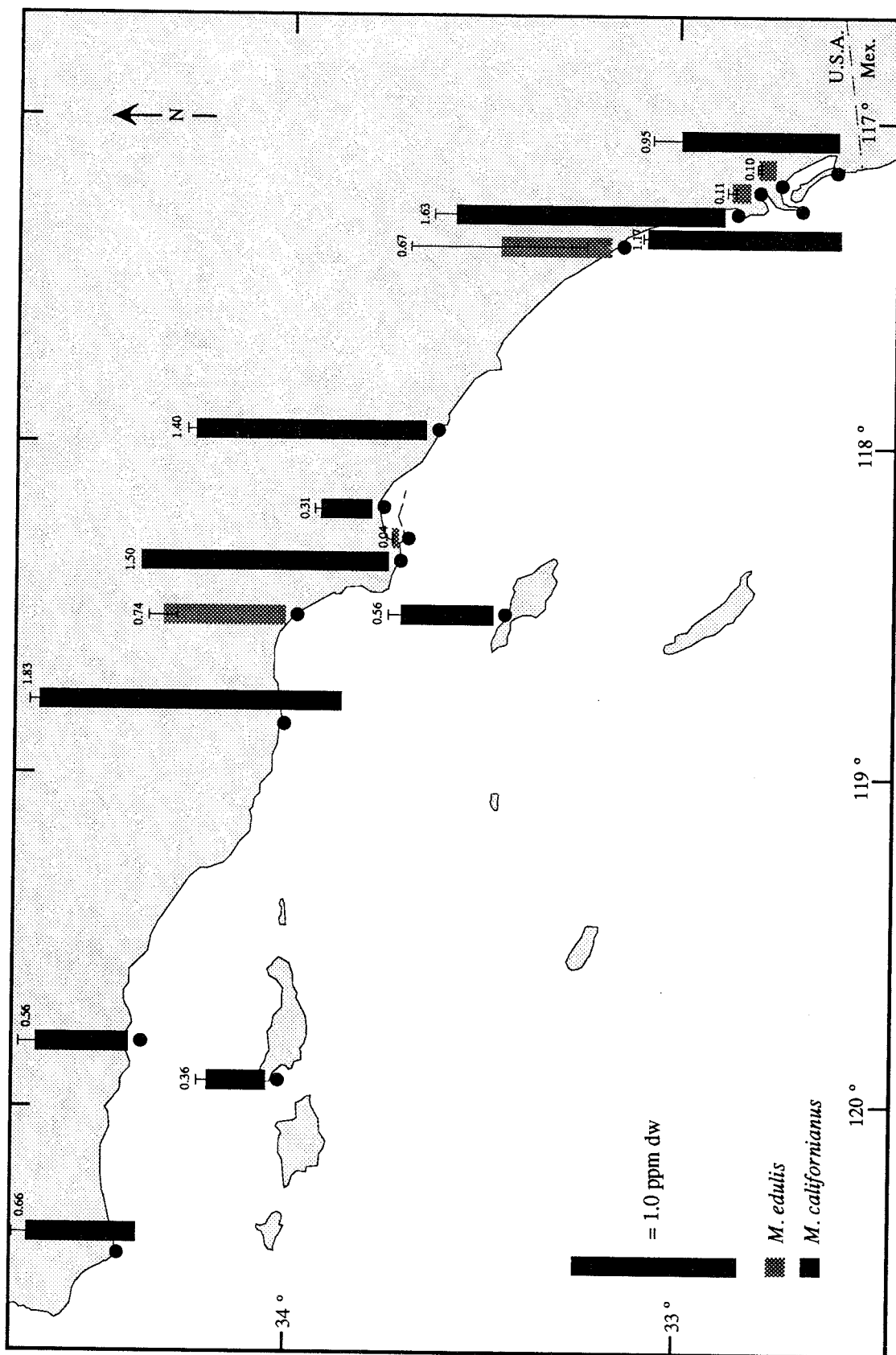
Figure 11.7. Silver in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

Table 11.3. Summary of silver concentrations (ppm dw) in whole *M. californianus* from various sampling areas in the southern California Bight, 1980 - 1986 (Phillips, 1988; NOAA, 1989).

Region or Site	Year	N	Mean	Median	Minimum	Maximum	Standard Deviation	Source*
All CMW	1977-85	123	7.74	2.61	0.04	64.0	11.74	CMW
Santa Monica Bay	1980	10	24.8	27.0	11.0	42.0	9.0	CMW
Santa Catalina Island	1980	5	0.82	0.35	0.19	2.52	0.98	CMW
Newport to Tijuana	1980	13	10.3	2.1	0.35	59.0	18.1	CMW
Point Dume	1986	3r	1.83	1.9	1.7	1.9		NS&T
Santa Barbara/Islands	1986	3	0.49	0.56	0.36	0.56		NS&T
Remaining NS&T coastal	1986	5	1.16	1.17	0.66	1.63	0.38	NS&T

* CMW - Phillips, 1988; NS&T - NOAA, 1989

Among the various harbors sampled by CMW and the NOAA NS&T Program, Marina del Rey showed high concentrations of silver. The mean of 0.69 ppm dw for two sites sampled by CMW in 1980 and 1982 is comparable to the 1986 NS&T Mussel Watch concentration of 0.73 ppm dw. Both means were considerably higher than the mean for the entire 1980-85 southern California CMW data set (0.12 ppm dw). By comparison, mean silver concentrations in *M. edulis* from Los Angeles-Long Beach harbors and from San Diego Harbor were low (0.10 and 0.15 ppm, respectively; Table 11.4).

Table 11.4. Summary of silver concentrations (ppm dw) in whole *M. edulis* from various sampling areas in the southern California Bight, 1980 - 1986 (Phillips, 1988; NOAA, 1989).

Region or Site	Year	N	Mean	Median	Min	Max	Standard Deviation	Source*
Channel Islands Harbor/ Oxnard	1980	1	0.05					CMW
Marina del Rey	1980, 1982	2	0.69	0.69	0.18	1.20		CMW
Marina del Rey	1986	3r	0.73	0.70	0.60	0.90		NS&T
Los Angeles/Long Beach harbors	1980, 1985	17	0.10	0.05	0.02	0.65	0.15	CMW
San Pedro breakwater	1986	3r	0.04	0.04	0.03	0.04		NS&T
Colorado Lagoon/ Seal Beach	1982, 1985	3	0.06	0.07	0.04	0.09		CMW
Anaheim Bay/Long Beach	1980, 1982	2	0.04	0.04	0.04	0.04		CMW
Newport Bay	1980, 1985	4	0.04	0.04	0.02	0.04	0.01	CMW
Newport Pier	1980	1	0.04					CMW
Oceanside Harbor	1985	1	0.07					CMW
Mission Bay	1980, 1982	5	0.04	0.05	0.04	0.22	0.08	CMW
Point Loma	1983	1	0.35					CMW
San Diego Harbor	1980, 1982	4	0.15	0.14	0.10	0.24	0.06	CMW
San Diego Harbor Island	1986	3r	0.10	0.09	0.08	0.12		CMW

r - replicate samples at the same site
* CMW - Phillips, 1988; NS&T - NOAA, 1989

Concentrations of silver in mussels from southern California have been higher than the overall mean concentration measured at NOAA's NS&T Program sites between 1984 and 1989. *M. californianus* contained a higher mean level of silver than *M. edulis* (0.628 ppm dw and 0.308 pm dw, respectively). Median values were 0.233 ppm dw for *M. californianus* and 0.155 ppm dw for *M. edulis*. The greatest site mean was found for *M. californianus* (0.5333 ppm dw).

There has been no significant change in silver content of mussels over the past 10 years. Long-term CMW trend data are available for only two sites, Royal Palms and Oceanside (Figure 11.8). Both sites were sampled approximately annually over the period 1977 through 1986. There was no significant (p >> 0.1) long-term trend at either site although there was a tendency for a decline at Oceanside ($r^2 = 0.354$). At Royal Palms, concentrations in *M. californianus* fluctuated between 3.0 and 9.5 ppm dw. At Oceanside, concentrations were much lower, ranging from 0.5 to 1.4 ppm dw but also with a long-term decrease from 1.4 ppm dw in 1977 to 0.2 ppm dw in 1983 followed by an increase to 0.8 ppm dw in 1986-87. The NS&T Program found so significant change in silver concentrations in mussels from southern California sites sampled between 1986 and 1988.

Despite the high concentration of silver in mussels from Royal Palms, it is difficult to show that variations in annual sewage inputs are controlling variations in the mussels. There was no significant correlation between silver mass emissions from the JWPCP outfall and concentrations in Royal Palms mussels sampled at the end of each discharge year. Indeed, there was a slight (but not statistically significant) inverse relationship between them. If variations in the silver content of mussels are influenced by variations in sewage, that influence may be on a short-term basis, such as might be caused by spikes of silver emissions occurring over several days or weeks.

SILVER IN FISH AND OTHER SPECIES

Silver in non-hepatic tissues of 31 species of fish and macroinvertebrates ranged from below detection (often 0.002 ppm ww) to 0.286 ppm dw in a yellow crab collected in 1976 from Dana Point (Table 11.5). The highest mean concentrations were in muscle of the yellow crab from Dana Point and Palos Verdes (0.196 ppm ww and 0.125 ppm ww), mantle of market squid from Santa Catalina Island (0.14 ppm ww) and whole mysids from Palos Verdes (0.14 ppm ww). The highest concentration in muscle of fish was 0.063 ppm ww in a white croaker from Dana Point (Table 11.5). In general, silver concentrations in fish muscle were below 0.01 ppm ww.

Unlike the case for concentrations of silver in sediments and mussels, there was very little evidence of bioaccumulation of silver in edible tissues of fish or macroinvertebrates collected in areas near silver contaminated sediments. Of five species of macroinvertebrates, two--black abalone and California spiny lobster--produced evidence of silver contamination near outfall sites. However, none of five species of fish exhibited such evidence (Table 11.6). In a statistical analysis of these and other data, Young *et al.*, (1978) concluded that median concentrations of silver in black abalone, rock (purple-hinge) scallop, and spiny lobster were approximately 3 times higher at Palos Verdes than at comparable control sites. However, data presented in Table 11.6 show the opposite trend for scallops due to the exclusion of 1974 data from Palos Verdes. Young *et al.* (1978) also confirmed the lack of sewage-related silver bioaccumulation in muscle of bony fish. Yellow crab accumulated silver at both sites where they were sampled. Based on these and other data, Young (1988) concluded that silver does not undergo biomagnification in marine organisms of the Southern California Bight, but may decrease with trophic level.

Silver was analyzed in livers of three species at six sites during NOAA'S 1984 NS&T surveys. Concentrations ranged from less than 0.02 ppm ww in livers of barred sand bass at Dana Point to about 0.7 ppm ww in livers of white croaker from the same site (Figure 11.9). Silver in liver of hornyhead turbot was highest in fish from Santa Monica Bay and lowest in fish from Dana Point (Figure 11.9). This was the only species and tissue of a fish that resulted in a geographic pattern reminiscent of the silver gradients in sediments and mussels.

There are no national or international action limits or criteria for silver in fish or fishery products (Nauen, 1983). Therefore, it is impossible to evaluate the significance of the concentrations reported here.
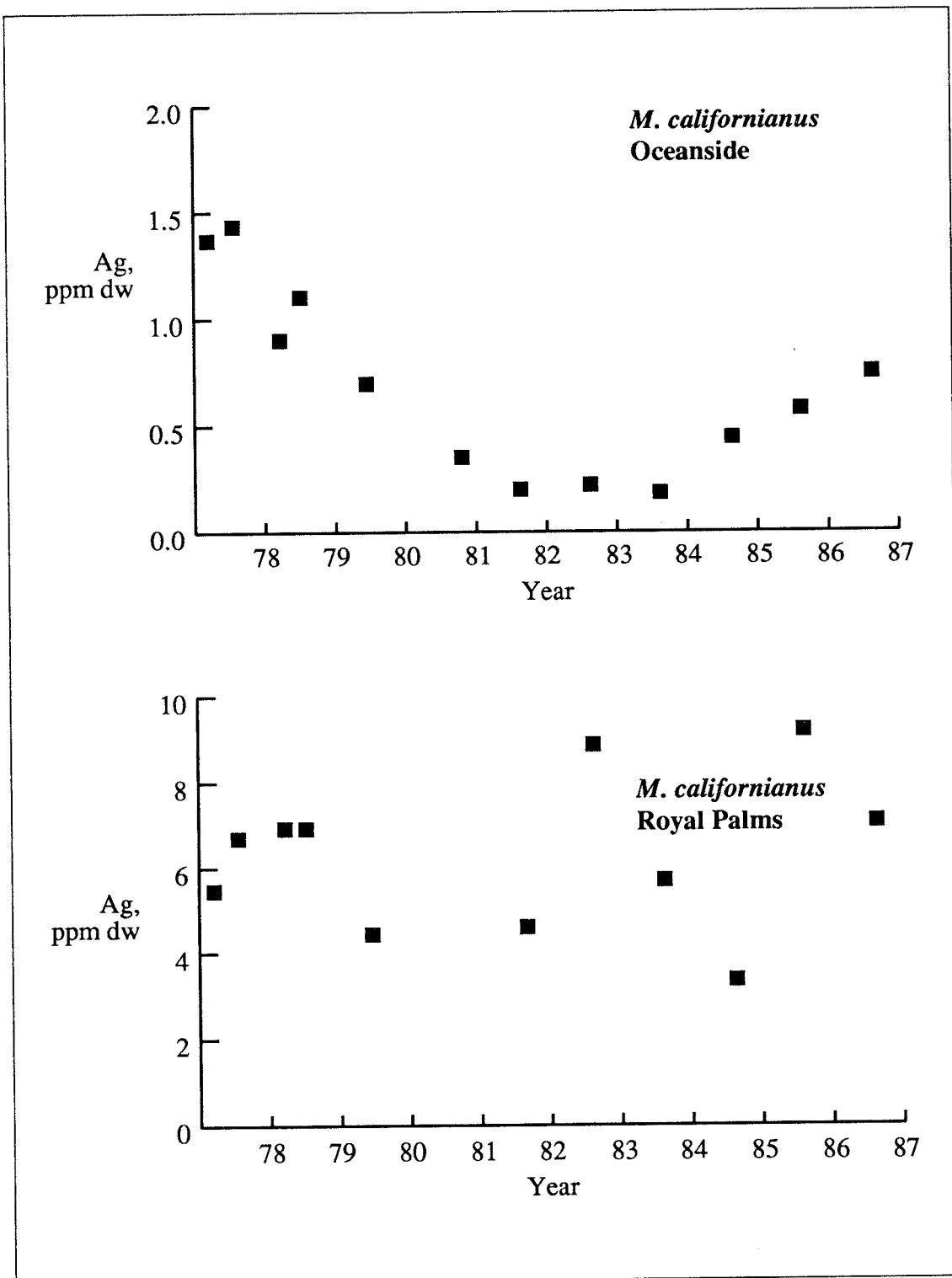
Figure11.8. Time series of silver in mussels sampled at Royal Palms and Oceanside 1977-87. Source: Phillips, 1988.

Table 11.5. Silver concentrations in edible tissues of marine organisms from the Southern California Bight.

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	Data Source
Kelp	Los Angeles Harbor	1979	5	0.005	0.005	0.004	0.006	0.001	Mearns and Young, 1980
Mysids	Palos Verdes	1980	8	0.140	0.014	0.051	0.242	0.056	Schafer et al., 1982
Zooplankton	Coastal	1980-81	5	0.044	0.046	0.014	0.074	0.024	Schafer et al., 1982
Black abalone	White Point	1976	3	0.031	0.018	<.008	0.060	0.028	Young et al., 1978
Black abalone	Santa Catalina Island	1975-77	3	0.010	0.007	<.005	0.020	0.009	Young et al., 1978
Gaper clams	Los Angeles Harbor	1979	5	0.015	0.010	0.001	0.032	0.013	Mearns and Young,1980
Markert squid	Coastal	1979	3	0.140	0.128	0.115	0.188	0.039	Shafer et al., 1982
Purple-hinge scallop	Santa Barbara	1973	2	0.011	0.011	0.060	0.015	0.006	Young et al., 1982
Purple-hinge scallop	Santa Catalina Island	1973-74	4	0.010	0.006	0.004	0.023	0.009	Young et al., 1982
Purple-hinge scallop	Palos Verdes	1976	8	0.006	0.002	<.002	0.027	0.009	Young et al., 1982
California spiny lobster	Santa Catalina Island	1977	3	0.015	0.014	0.009	0.023	0.007	Young et al., 1978
California spiny lobster	San Diego	1977	3	0.017	0.020	0.008	0.023	0.008	Young et al., 1978
California spiny lobster	Royal Palms	1978	3	0.040	0.058	<.004	0.059	0.033	Young et al., 1978
Ridgeback prawn	Palos Verdes	1976	3	0.003	0.002	<.004	0.006	0.002	Young et al., 1978
Ridgeback prawn	Orange County	1975	3	0.023	0.023	<0.002	0.046	0.023	Young et al., 1978
Ridgeback prawn	Dana Point	1975-77	3	0.006	0.005	0.001	0.010	0.004	Young et al., 1978
Ridgeback prawn	Palos Verdes	1980	5	0.001	0.001	0.001	0.001	0.002	Shafer et al., 1982
Yellow crab	Bunker Point	1975-76	3	0.125	0.095	0.087	0.193	0.059	Young et al., 1978
Yellow crab	Dana Point	1976	3	0.196	0.219	0.084	0.286	0.103	Young et al., 1978
Bocaccio	Palos Verdes	1976	3	0.006	0.008	<.003	0.009	0.004	Young et al., 1978
Bocaccio	Orange County	1976	3	0.005	0.005	0.003	0.006	0.002	Young et al., 1978
Bocaccio	San Clemente Island	1977	3	0.005	0.003	<.005	0.011	0.005	Young et al., 1978
California halibut	Palos Verdes	1976	2	0.002	0.002	<.003	<.003	-	Young et al., 1978
California halibut	Point Dume	1976	2	<.003	<.003	<.003	<.003	-	Young et al., 1978
California halibut	Los Angeles Harbor	1979	4	0.001	0.001	0.001	0.001	0.000	Mearns and Young, 1980
California halibut	Pointt Dume	1976	2	0.001	0.002	0.002	0.002	0.000	Young et al., 1978
California scorpionfish	Palos Verdes	1976	3	0.019	0.022	0.012	0.024	0.006	Young et al., 1978
California scorpionfish	Orange County	1974-75	3	0.026	0.025	0.017	0.036	0.100	Young et al., 1978
California scorpionfish	Dana Point	1975-77	3	0.025	0.023	0.023	0.028	0.003	Young et al., 1978
California scorpionfish	Palos Verdes	1980	4	<.003					Schafer etal, 1982
Dover sole	Palos Verdes	1980	5	0.008	0.001	0.001	0.001	0.000	Schafer etal, 1982
Northern anchovy	Los Angeles Harbor	1979	5	0.001	0.001	0.001	0.002	0.001	Mearns and Young, 1980
Northern anchovy	Coastal	1980-81	5	0.010	0.010	0.014	<.002	0.020	0 Schafer etal, 1982
Pacific bonito	Coastal	1980-81	5	<.003					Schafer etal, 1982
Pacific hake	Coastal	1980-81	5	0.002	<.002	<.002	<.002	--	Schafer etal, 1982
Pacific mackerel	Coastal	1980-81	6	0.003	0.003	<.002	0.004	0.001	Schafer etal, 1982
Pacific sanddab	Santa Catalina Island	1973	3	0.030	0.003	<.004	0.005	0.002	Young et al., 1978
Pacific sanddab	Palos Verdes	1976	3	0.006	0.005	<.004	0.010	0.004	Young et al., 1978
Pacific sanddab	Orange County	1977	3	0.002	0.002	<.004	<.005	0.000	Young et al., 1978
Pacific sanddab	Dana Point	1976	3	0.006	0.002	<.001	0.014	0.007	Young et al., 1978
Pacific sardine	Coastal	1980-81	5	<.003	<.003	<.003	<.003	--	Schafer etal, 1982
Spotted sand bass	Newport Bay	1978	3	0.003	0.003	0.002	0.004	0.001	MBC and SCCWRP, 1980
Striped bass	Newport Bay	1978	3	0.003	0.003	0.002	0.004	0.001	MBC amd SCCWRP, 1980
Striped mullet (adult)	Newport Bay	1978	3	0.002	0.001 <.002	<.003		0.001	MBC and SCCWRP, 1980
Striped mullet (juvenile)	Newport Bay	1978	3	0.002	0.002	0.002 <.003		0.00	MBC and SCCWRP, 1980
Swordfish	Coastal	1980	5	<.002	<.002	<.002	<.002	--	Schafer etal, 1982
Topsmelt	Newport Bay	1978	3	0.002	0.001 <.002		0.003	0.001	MBC and SCCWRP, 1980
White croaker	Palos Verdes	1977	3	0.022	0.019	0.016	0.032	0.009	Young et al., 1978
White croaker	Orange County	1975	3	0.027	0.031	0.018	0.031	0.008	Young et al., 1978
White croaker	Dana Point	1976	3	0.036	0.023	0.022	0.063	0.023	Young et al., 1978
White croaker	Los Angeles Harbor	1979	5	0.004	0.004	0.003	0.006	0.001	Mearns and Young, 1980
White croaker	Palos Verdes	1980	5	0.001	0.001	0.001	0.001	0.00	Schafer etal, 1982
Yellowfin croaker	Newport Bay	1978	3	0.002	0.003 <.002		0.003	0.001	MBC and SCCWRP, 1980
Mako shark	Coastal	1980-81	5	0.006	0.006	0.002	0.011	0.003	Schafer etal, 1982
Spiny dogfish	Palos Verdes	1980-81	5	evel (.002)					Schafer etal, 1982
Thresher shark	Coastal	1980-81	5	evel (.002)					Schafer etal, 1982
White shark	Coastal	1980-81	3	<.002	<.002	<.002	<.002	--	Schafer etal, 1982

Table 11.6. Mean concentrations and standard deviation of silver (ppm ww) in edible tissue of 10 popular seafood organisms collected in 1975 through 1978 (based on data supporting Young *et al.*, 1982). Number of samples is shown in parentheses.

COMMON NAME	SANTA BARBARA	VENTURA/ POINT DUME	PALOS VERDES	LOS ANGELES HARBOR	ORANGE COUNTY	DANA POINT	SAN DIEGO	SANTA CATALINA	SAN CLEMENTE
Black abalone			0.031 ±0.028 (3)					0.010 ±0.009 (3)	
Purple-hinge scallop	0.011 ±0.015 (2)		0.006 ±0.027 (8)					0.010 ±0.023 (4)	
Yellow crab			0.125 ±0.059 (3)			0.196 ±0.103 (3)			
California spiny lobster			0.040 ±0.033 (3)				0.017 ±0.008 (3)	0.015 ±0.007 (3)	
Ridgeback prawn			0.003 ±0.002 (3)		0.023 ±0.046 (3)	0.006 ±0.004			
Pacific sanddab			0.006 ±0.004 (3)		0.002 ±0.000 (3)	0.006 ±0.007 (3)		0.003 ±0.002 (3)	
California halibut		<0.003 (2)	0.002 ±0.000 (2)	0.001 ±0.000 (4)					
White croaker			0.022 ±0.009 (3)	0.004 ±0.001 (5)	0.027 ±0.008 (3)	0.036 ±0.027 (3)			

Table 11.6 (continued)

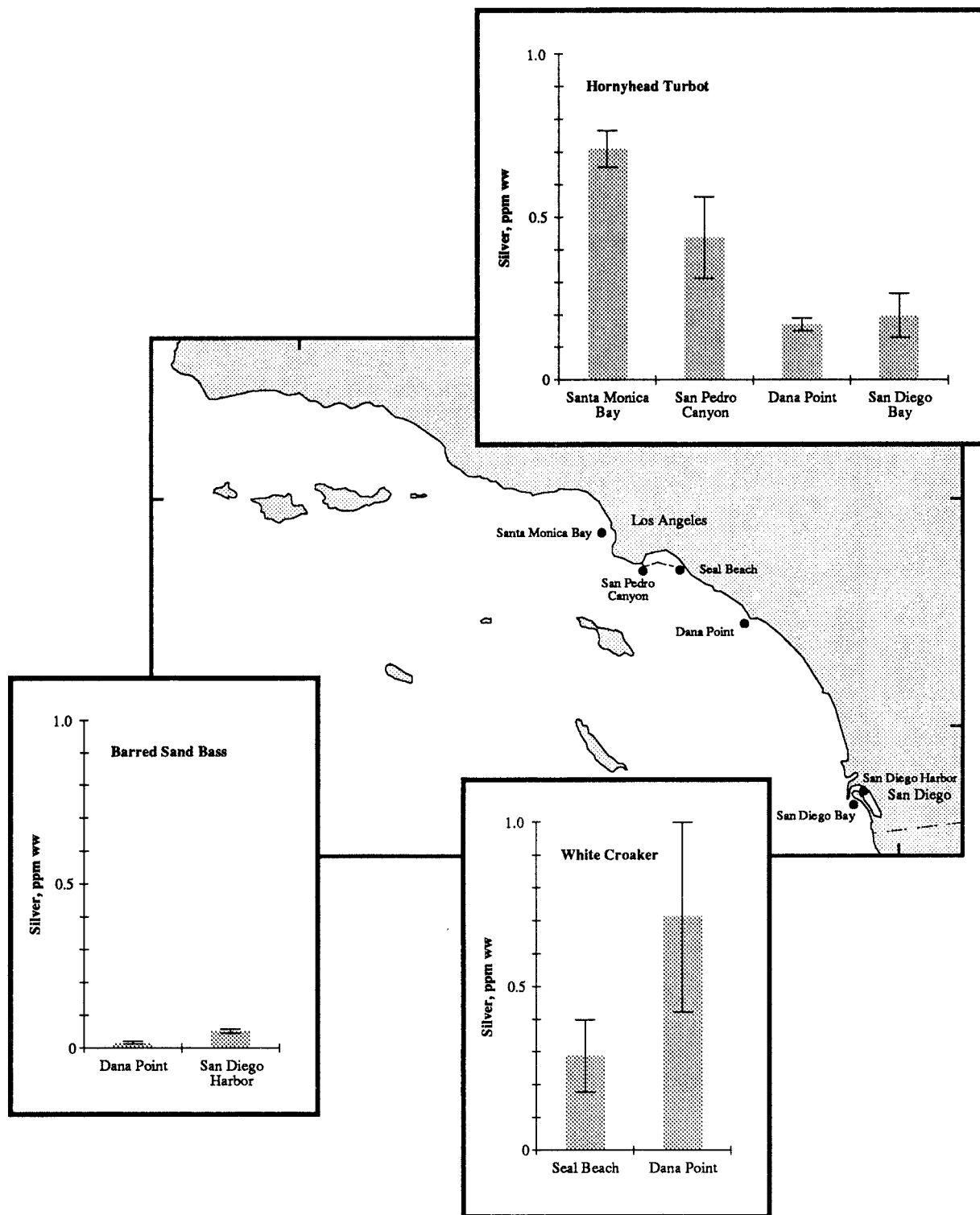| COMMON NAME	SANTA BARBARA	VENTURA/POINT DUME	PALOS VERDES	LOS ANGELES HARBOR	ORANGE COUNTY	DANA POINT	SAN DIEGO	SANTA CATALINA	SAN CLEMENTE
Bocaccio			0.006 ±0.004 (3)		0.005 ±0.002 (3)				0.005 ±0.005 (3)
California scorpionfish			0.019 ±0.006 (3)		0.023 ±0.010 (3)	0.025 ±0.003 (3)			

Figure 11.9. Concentrations of silver measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

SUMMARY AND CONCLUSIONS

Silver is a difficult contaminant to evaluate. Dated cores show that silver concentration in sediments of the Southern Califronia Bight began increasing between 1940 and 1960. Inputs appear to be dominated by sewage and increased or remained relatively unchanged during the late 1970s and early 1980s. Sediments near discharge sites and in at least one harbor area were contaminated with silver during this time. Concentrations in *M. californianus* exhibited a very large-scale gradient of contamination radiating out of the Los Angeles and San Diego areas into Mexico and central California. This is reminiscent of the DDT gradient (chapter 15). There was also evidence of local contamination of some other macroinvertebrates near Palos Verdes discharge sites, but not in muscle tissue of fish. Lack of data on fish from some harbors and from Mexico and central California precludes assessing whether the large-scale gradient in mussels also occurs in fish. There is no evidence that silver undergoes biomagnification. Lack of action limits or criteria prevent evaluating the significance of past or current levels, even where accumulation in mussels and other macroinvertebrates was observed.

Sediment surveys suggest that silver contamination is generally localized around discharge areas, but surveys of mussels suggest a much larger scale distribution has occurred. These disparate results might be tenable if, unlike other metals, silver could be viewed mainly as a dissolved or suspended water column contaminant, accumulating in sediments only where deposition rates have been extraordinarily high such as at Palos Verdes (Kettenring, 1981) or in Santa Monica submarine canyon. Unfortunately, the thermodynamics and ecological behavior of silver in the Southern California Bight have not been investigated.

INFORMATION NEEDS

If silver is indeed a useful measure of sewage contamination and, if, as seems to be the case, inputs have not been substantially controlled (as have other contaminants), there is great need to understand more about its sources, cycling, and potential effects. Mussel and sediment time series need to be re-instituted. Harbors, marinas, and sites near rivers and flood control channels need to be monitored. The form and potential toxicological implications of high concentrations in filter-feeding organisms need to be understood. Industrial and domestic sources should be evaluated and controlled if the concentrations that have been observed in mussels and crab are at levels of concern. Reference or background levels in sediments should be confirmed so that regulatory agencies will know when controls have been successful. The fate of silver in sediments should be explored.

CHAPTER 12

TIN AND ORGANOTIN

Tin has been a relatively common element of industry and commerce since ancient times, but, during the 1980s, organic tin compounds, mainly tributyltin (TBT), have received great scrutiny as potent toxins to some forms of marine life, especially mollusks.

Tin is used for metal plating, in food packaging and textile dyes, and as a component of solder, bronze, pewter, brass, perfume stabilizers, catalysts, and fluoride toothpastes. Organic tin formulations (organotins) have been used as insecticides, molluskicides, bactericides, and fungicides; in vessel paints to prevent fouling of hulls; and as stabilizers, curing agents, and catalysts in industrial chemistry (Goyer, 1986; Magos, 1986; Eisler, 1989).

According to data reviewed by Eisler (1989), current worldwide reserves of tin are 6.5 million tons. Annual production in 1975 was 236,000 mt, mostly from mines in Asia; western nations recycled 20,000 mt. While most of the produced tin has been used in inorganic forms (tinplate, solder), industrial consumption of organotins rose from 5,000 mt in 1965 to about 35,000 tons in 1980 of which 67 percent (22,750 mt) was in "nontoxic" (mono- and di-organotin) compounds and the balance (12,250 mt) in the toxic (triorganotin) forms (Eisler, 1989).

The literature is somewhat confusing about use of the terms that describe tin and tin compounds in environmental samples. Elemental, inorganic, and organic forms of tin exist in nature or are produced by man. The **total tin** reported for foods and other biological samples is that tin either extracted using various inorganic acids followed by AAS, or the tin (presumably all) responsive to emission spectroscopy or neutron activation analysis of unextracted tissues (World Health Organization [WHO], 1980). It may include both organic and inorganic compounds. From 3 to 52 percent of the total tin in fish and from 35 to 75 percent of the total tin in limpets is in the form of organic tin (Eisler, 1989). Organic tin compounds include **methyltin** compounds, which are both natural and man-produced, and **butyltins**, which are completely synthetic. Tissues and sediments from the Southern California Bight have been analyzed for total tin and various organotin compounds (mainly butyltins and methyltins), but rarely for both groups in the same samples. Sometimes, just tin is reported; when that is the case, it was assumed that this is equivalent to total tin for this review.

Although there is evidence that inorganic tin interferes with calcium metabolism at relatively high doses, Magos (1986) and Eisler (1989) conclude that inorganic tin and its salts are relatively harmless (nontoxic) except when leached from canned food. Tin is an essential trace element in rats and its elimination from diet reduces growth. However, some organotin compounds are very toxic. Qualitative and quantitative toxicities vary among specific compounds, animal species, and developmental stages; and the di- and tri-alkyl tins are apparently the most toxic. Significantly, microbial flora present in estuarine sediments have been found to be capable of transforming inorganic tin (Sn IV) into methyl tins (Cooney and Hallas, 1981). Interference with cellular enzyme biochemistry (inhibition of hydrolysis of adenosine triphosphate and uncoupling of oxidative phosphorylation) has been suggested as a mechanism of tin toxicity (WHO, 1980; Goyer, 1986; Magos, 1986).

It appears that in the marine environment, bioavailability of organotins may be influenced by a number of physical and chemical factors, especially those affecting complexation and adsorption. Salazar (1986) noted that TBT associated with particulate material is an important route of exposure for suspension-feeding organisms. Laughlin (1986) found that TBT bioaccumulated in all organisms at all phylogenetic and trophic levels, and that environmental factors had little mitigating effect. Concentration factors referred to by Laughlin included 2000 and 6000 (in high and low dissolved concentrations, respectively) for the oyster *C. gigas*, 1000 and 1500 for the oyster *O. edulis*, and 30,000 for the phytoplankton species *Ankistrodesmus falcatus*. In *M. edulis*, exposure to dissolved TBT concentrations of 23 and 45 parts per trillion (ppt) resulted in a maximum tissue burden of 70 ppb ww after 12 to 14 days.

An important question is the extent to which total tin measurements in tissues or sediments also record accumulations of tin from organotin compounds. A modest historical data base for total or inorganic tin exists, and if there is a relationship between inorganic and organic tin, then careful examination of total or

inorganic tin data may reveal where levels of organotin may have been increasing in the past. Furthermore, although butyltins degrade relatively quickly, it may be that inorganic and total tin do not.

Data from Davies and McKie (1987) help answer this question. They exposed groups of Atlantic salmon (*Salmo salar*) to differing concentrations of TBT in water for a 26-day period, then measured the accumulated concentrations of total tin and organotin in various body tissues, including muscle and liver. With increasing TBT concentration, concentrations of total tin increased in all organs. In addition, the ratio of total tin in liver to total tin in muscle increased from about 0.5 to 5.2 (Figure 12.1) indicating that liver was a much more responsive organ for bioaccumulation. At the control exposure after 26 days, concentrations of tin in muscle measured 0.07 ppm ww and in liver measured 0.04 ppm ww. At the highest exposure of 1.0 ppb TBT, muscle tissue contained 0.31 ppm, while liver contained 1.62 ppm In short, it appears that measures of total tin can reflect bioaccumulation of organotins, particularly in liver of fish.
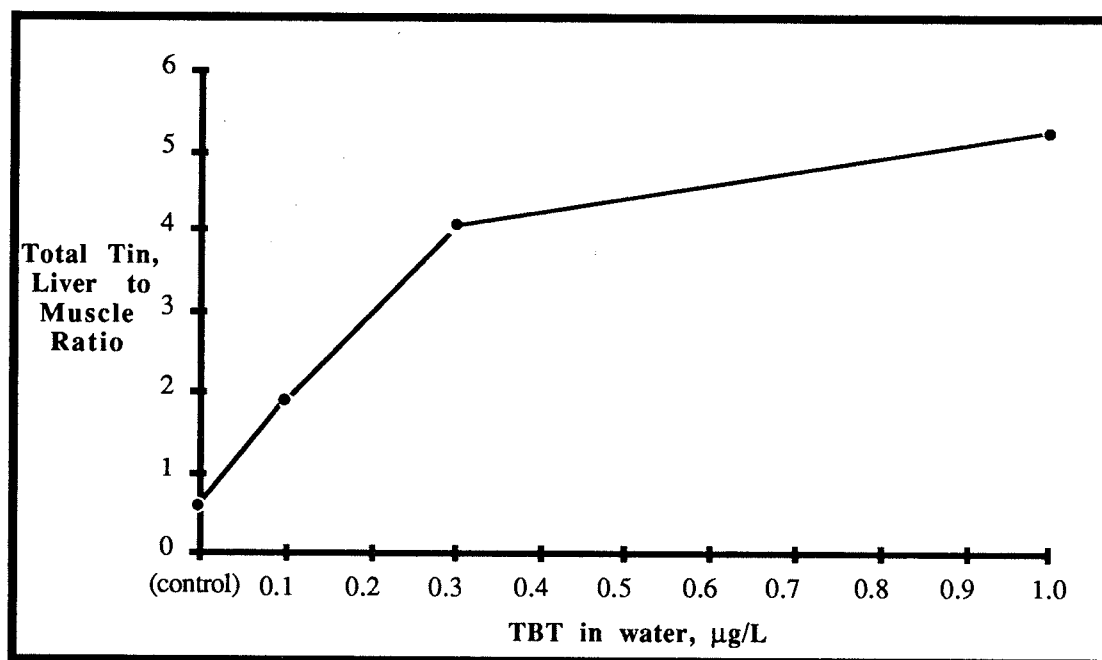

Figure 12.1. Increase in the ratio of total tin in liver to total tin in muscle of juvenile Atlantic salmon with increasing concentrations of TBT in water. Developed from data in Davies and McKie (1987).

Most toxicity studies have focused on TBT in water. Rexrode (1987) summarized results for acute and chronic toxicity of TBT among a number of different biota. Sensitivity to exposure in water was found to vary among aquatic species; with mysids, gastropods, and bivalves among the most susceptible. Fish species (mostly freshwater) were least sensitive, with adverse impacts noted at TBT concentrations greater than 0.2 ppb. Even lower concentrations of TBT damage bivalve mollusks. Although the 48-hour (short-term) LC_{50} for *M. edulis* is 2.5 ppb TBT (Thain, 1983, as cited in Cleary and Stebbing, 1985), lethal and sublethal effects occur to oyster, clam, and mussel larvae at concentrations ranging down to 0.01 ppb (Beaumont and Budd, 1984; Stroemgren and Bongard, 1987; Thain, 1986; and Lawler and Aldrich, 1987). Although TBT concentrations in coastal waters of the Southern California Bight were generally below 0.01 ppb, concentrations in waters of most marinas were well within the range of sublethal and lethal toxicity (Stallard *et al.*, 1987).

Manifestation of toxic effects at such low concentrations (ppt level) distinguishes organotins, and specifically TBT, as being among the most potent marine toxicants identified. In addition to problems intrinsic to measurement of analytes at these extremely minute concentration levels, analyses of organotin concentrations have been made even more difficult by the inability, until recently, to extract reliably and determine tin species in mixtures containing both inorganic and organic tin (WHO, 1980). Lawler and Aldrich (1987) commented that impacts at even lower levels may be masked by experimental errors.

Sources of tin to the ocean or the Southern California Bight are not quantified. Potentially important sources of total and organic tins could include efflux from vessel paint, sewage, industrial discharges, and even aerial fallout. Annual total tin flux in the atmosphere is about 8 times higher in the northern hemisphere (17,000 mt per year) than in the southern hemisphere (2300 mt per year). Most of this flux (90%) is of human origin and the most important source, according to data reviewed by Eisler (1989), is incineration of municipal waste.

Probably the most important measured anthropogenic source of organotins to the marine environment is antifouling coatings on vessel hulls, in which organotin is an active ingredient. Tin was first employed in vessel antifouling paints in the early 1960s and its effectiveness in reducing biotic growth on recreational, commercial, and military hulls caused its use to grow steadily. In 1987, it was estimated that organotin-based antifouling paints accounted for 58 percent of annual antifouling paint sales, or greater than 800,000 gallons (Ludgate, 1987). There is no direct estimate of the amount of TBT paint used in the Southern California Bight. Champ and Bleil (1988) estimated that the United States' annual use of TBT in antifouling paints was approximately 624,000 gallons with over 1,000,000 pounds (450,000 kilograms [kg]) of TBT. Citing additional data, they note an annual use along the Pacific Coast of 218,300 gallons of paint containing TBT. This is about one-third of the total United States' usage in gallons and could represent about 154,400 kg of TBT (or about 157 mt per year for the Pacific Coast). Physical mechanisms of organotin input associated with these paints include the leaching that forms the basis of their effective properties, and, near vessel repair facilities, hull washing, sandblasting, scraping, and painting activities. For example, paint scrapings from five Newport Bay shipyards contained tin concentrations ranging from 360 to 2400 ppm dw (median, 480 ppm; Liu and Schneider, 1988) while those from the San Diego Shelter Island Commercial Basin were in the range of 170 to 250 ppm dw (Stephenson *et al.*, 1988).

No data were encountered for determining mass emission rates of tin or organotins to the Southern California Bight from sewage, industrial discharges, runoff, or other sources. Concentrations of total tin in the range of 18 to 79 µg per liter and 7 to 60 µg per liter were reported for influents to the San Francisco Southeast (30 MGD) and Northpoint (65 MGD) sewage treatment plants (STPs) respectively, in a series of seven 24-hour composites taken in April 1973 (City and County of San Francisco, unpublished data). These translate into a combined (95 MGD) mass input rate of 2.25 mt tin per year. Extrapolating to 1,300 MGD for Southern California Bight sewage effluents result in an overall estimate of 30.8 mt per year entering southern California STPs annually in untreated sewage. Treatment (primary and secondary) could lower this substantially (by a factor of 5 or 10) if tin were largely absorbed to particulate material. Thus, past inputs from southern California sewage might have been somewhat under 30 mt per year while current inputs might be about 3 to 6 mt per year. Although these represent only about 0.01 percent of the global riverine flux, they may, nevertheless, be significant relative to other regional sources of tin. Since incineration of sewage wastes is a major source to the atmosphere, and since the form(s) of tin in sewage remain unknown, it is important not to rule out all types of sewage processes as potential major sources of total tin or organotins to the Southern California Bight.

In view of this, analytical and regulatory problems related to the use of organotin compounds become obvious. In 1982, France prohibited the use of organotin paints on all boats less than 25 meters long. In 1986, Great Britain banned the use of paints with greater than a specified organotin concentrations (2.5 to 7.5%, depending on paint formulation (Huggett, 1987). In the United States, a number of state legislatures passed measures regulating the use of organotin-based paints. Finally, Federal legislation based on organotin release rates restrictions was passed in 1988. Paints with release rates greater than 4 µg TBT per square cm per day are prohibited, and vessels less than 25 meters long are not permitted to use TBT-based paints unless they are aluminum hulled. Effective alternatives to tin-based antifouling paints on aluminum hulls are not currently available.

TIN IN SEDIMENT

Total Tin

Sediments from the Southern California Bight have been measured for total tin or Sn IV since 1974 (Young et al, 1975; Seidel et al, 1980, and NOAA, 1988). Concentrations ranged from 0.07 ppm dw in a sample from Carpinteria Lagoon in 1979 (Seidel et al, 1980) to 89.0 ppm dw from the commercial basin of San Diego Harbor in 1974 (Young et al, 1975). The results of all surveys indicate that concentrations have been at least an order-of-magnitude higher in urban bays than in rural lagoons or at open coastal sites. However, absolute concentrations are not comparable among these data sets and it is difficult to judge "normal" or "background" concentrations. Sedimentary rocks may contain up to 30 ppm total tin (Purves, 1985).

In an April 1974 survey at 11 transects in San Diego Harbor (Young et al., 1975) mean concentrations of total tin in replicate surface sediments ranged from less than 20.0 to 53.5 ppm dw with an overall mean and median of 36.8 and 36.5 ppm dw, respectively. Individual surface concentrations of total tin ranged from less than 20 ppm dw to 89 ppm dw. The median concentration for four transects at the commercial basin at the northwestern corner of the harbor was 47.7 ppm dw (range 37.0 to 53.5). It was 30.3 ppm dw (28.0 to 32.6) at two transects near the commercial docks south of the downtown area, 19.6 ppm dw (less than 20 to 29.2) at the National Steel and Shipbuilding Company and 36.5 ppm dw (36 to 47.2) at the naval station.

Subsequent surveys produced much lower concentrations than those reported in Young et al. (1975). In 1979, Seidel et al. (1980) conducted a survey of Sn IV and monobutyl tin in sediments from 22 sites in southern California as part of a 36-site statewide survey. Tin (Sn IV) concentrations ranged from 0.07 ppm dw at Carpinteria Marsh to 11.08 ppm dw at a site in inner Los Angeles-Long Beach harbors. Concentrations at four sites in San Diego Harbor ranged from 0.46 to 4.26 ppm dw, far below the 20 to 60 ppm range reported in the 1974 survey (reported by Young et al., 1975). Nonetheless, concentrations were higher in the urban bays and harbors (San Diego Harbor, 0.46 to 4.26 ppm dw; Los Angeles-Long Beach harbors, 1.18 to 11.00; Mission Bay, 0.95 to 2.64) than in six undeveloped southern California bays and lagoons (0.07 to 0.47 ppm dw; Table 12.1).

Mean concentrations of total tin at six sites sampled during the 1984 and 1985 NS&T Program Benthic Surveillance surveys ranged from 0.55 ppm dw at a site in southern Santa Monica Bay to 11.8 ppm dw at a site in San Diego Harbor, both in 1985. As shown in Figures 12.2 and 12.3, intermediate concentrations (2 to 6 ppm dw) were reported in Long Beach Harbor, San Pedro Canyon, and San Diego Bay, as well as in San Diego Harbor (in 1984 only).

The NS&T Program Mussel Watch Project results for sediments in 1986 and 1987 are less easily interpreted than those of the Benthic Surveillance Project due to higher limits of detection. Of 62 southern California sediment samples analyzed from collections made in 1986 and 1987, only six concentrations were above limits of quantification ranging from 1.7 to 5.2 ppm dw. Five of the six measurements high enough to be quantified originated in the two areas also noted by 1984 and 1985 Benthic Surveillance Project analyses as having relatively high concentrations of tin in sediments (San Diego Harbor and the San Pedro-Palos Verdes Peninsula region). The consistently high concentrations at the Palos Verdes/Royal Palms site in 1987 (mean 11.6 ± 3.14 ppm) are somewhat surprising, and may indicate that the Whites Point JWPCP discharge outfall was a source of tin to nearby sediments (Table 12.1).

It is possible differences in methods were the cause of differences among the three surveys (Table 12.1) for ranges of total tin. The lowest values, reported by Seidel et al. (1980) were produced using only hydrochloric acid extracts. The NS&T Program samples were extracted with nitric acid and hydrofluoric acid, which would tend to produce higher values. However, no samples were taken in shipyards or marinas or near known specific tin sources. It is not clear how sediments from the 1974 San Diego Harbor survey were extracted, but they were clearly collected in and around areas of ship and vessel activity, which could explain, in part, why these values were so high then. The overall mean level of total tin in sediments measured by NOAA's NS&T Program between 1984 and 1989 was 2.814 ppm dw (median 1.436 ppm dw). The highest site mean value was 74.167 ppm dw.

Table 12.1. Summary of total (inorganic) tin concentrations in sediments from three surveys in the Southern California Bight, 1974-85.

Area	Year	N	Mean	Median	Minimum	Maximum	Data Source
San Diego Harbor	1974	11[a]	36.8	36.5	<20.0	89.0	1
San Diego Harbor	1979	4	1.83	0.74	0.46	4.26	2
Mission Bay	1979	4	1.50	1.20	0.95	2.64	2
Los Angeles-Long Beach harbors	1979	8	3.12	1.72	1.18	11.08	2
6 lagoons (southern California)	1979	6	0.19	0.14	0.07	0.47	2
Morro Bay (central California)	1979	3	0.17	0.18	0.14	0.19	2
San Francisco Bay	1979	8	3.83	3.41	0.59	10.41	2
Halfmoon Bay (central California)	1979	1	0.33	–	–	–	2
6 southern California sites [b]	1984	6	2.90	2.19	1.14	5.95	3
6 southern California sites [b]	1985	6	3.94	2.70	0.55	11.8	3
San Diego-Harbor Island [c]	1986	2	4.45	4.45	2.8	6.09	3
Point Santa Barbara [c]	1986	1	4.08	–	–	–	3
Palos Verdes [c]	1987	3	11.5	12.3	8.16	14.3	3

[a] Each site includes various depths and replicates

[b] Descriptive statistics based on means of triplicates

[c] Descriptive statistics only for positive samples; below detection data not included.

1. Young *et al.* (1975)
2. Seidel *et al.* (1980)
3. NOAA (1988)

As a result of incomparable methods and specific sites in past surveys, it is not possible to judge long-term trends of tin contamination in the Southern California Bight from these surveys. However, Seidel *et al.* (1980) measured total tin at 1- to 3-cm intervals in a core collected from Mission Bay in 1979. Concentrations varied from less than 0.1 to 1.1 ppm dw below 6 cm then increased to 1.8 ppm dw at the surface. Concentrations at the deepest part of the core (21 to 32 cm) varied between 0.6 and 0.8 ppm dw. This range is close to the lowest mean concentration of 0.55 ppm dw found in the 1984 NS&T Program Benthic Surveillance samples from Santa Monica Bay, and may suggest of a "background" total tin concentration for nearshore areas of the Bight about 0.5 ppm.
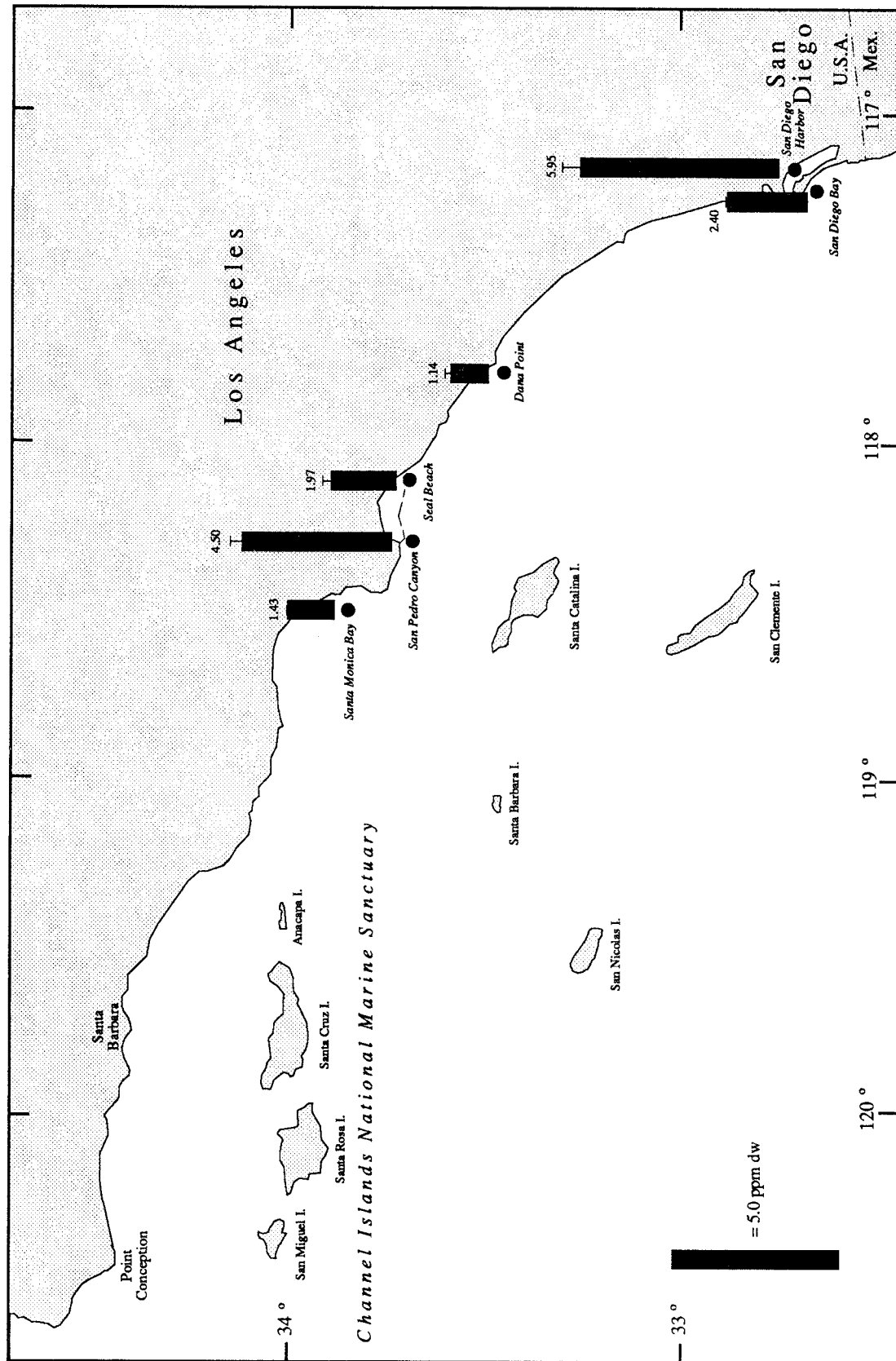
Figure 12.2. Concentrations of tin measured in sediments of the Southern California Bight in 1984. Values shown are means of three sample composites. Source: NOAA, 1988 and NOAA unpublished data
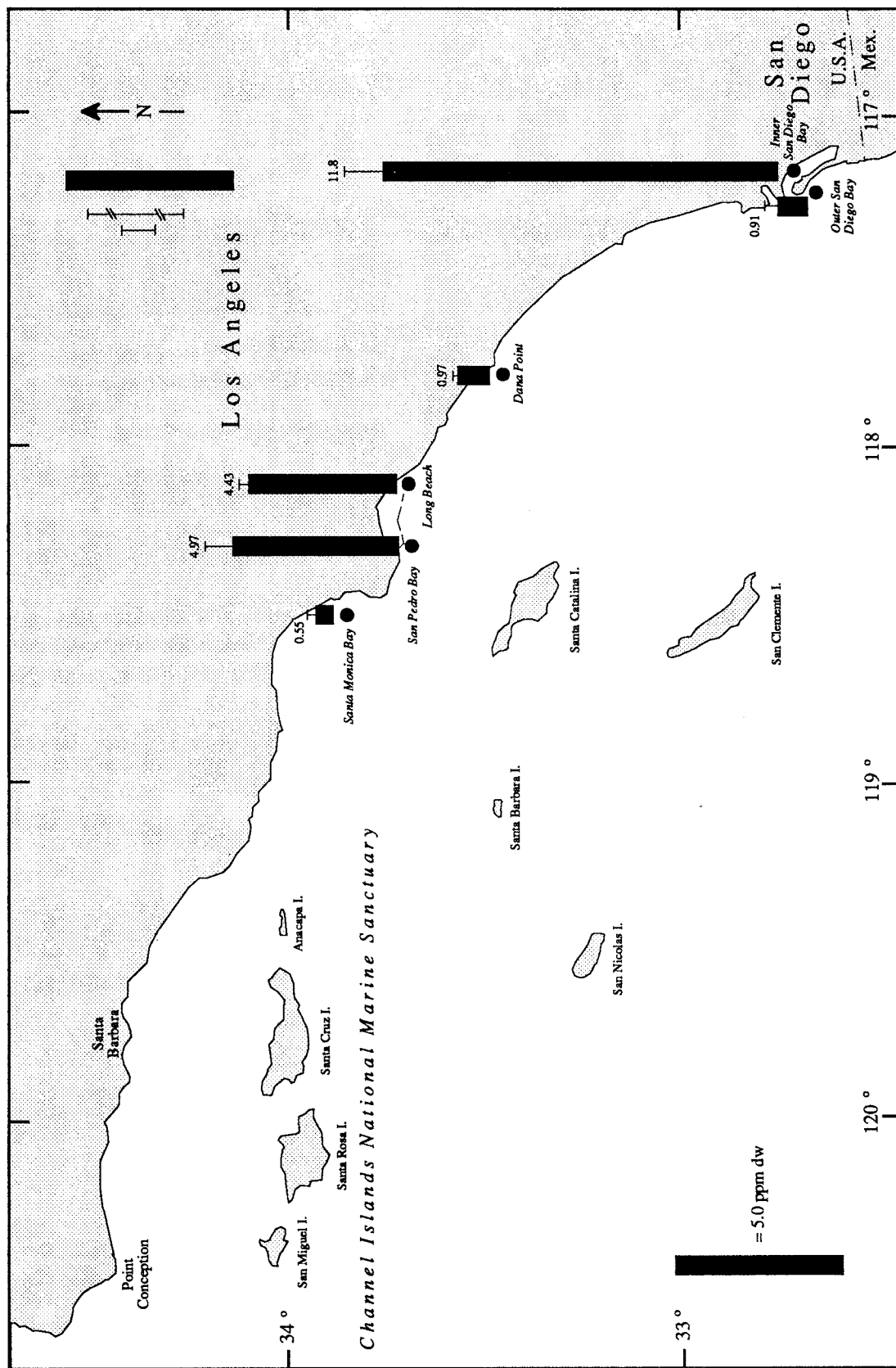
Figure 12.3. Concentrations of tin measured in sediments of the Southern California Bight in 1985. Values shown are means of three sample composites. Source: NOAA, 1988 and NOAA unpublished data.

Organotins

Organotin compounds in sediments usually occur in the ppb range whereas, total (and inorganic) tin occurs in the much higher ppm range.

Monobutyl tin (MBT) was the first organotin compound searched for in sediments from the Southern California Bight. In a 1979 survey of sediments from 22 southern California sites, Seidel *et al.*, 1980 reported concentrations ranging from less than 0.0004 ppm dw at 13 sites to 0.123 ppm dw both at Spanish Landing in San Diego Harbor and Rose Inlet in Mission Bay.

The U.S. Navy sponsored several studies in the San Diego region to provide information relevant to possible military use of organotin-based antifouling paints on the large numbers of vessels stationed in San Diego Harbor. Stang and Seligman (1986) studied distribution and fate of butyltin compounds in sediments collected in 1984. Valkirs *et al.* (1986) incorporated these sediment values along with water concentrations as part of a comparison of partitioning coefficients calculated from particulate and water concentrations. They found mean total butyltin concentrations in sediments of 0.228 ± 0.065 ppm dw in the Shelter Island Yacht Basin and 0.445 ± 0.418 ppm in the Shelter Island Commercial Basin. Near a commercial drydock facility, sediment concentrations of 0.062 to 0.100 ppm were measured. In all cases, butyltin concentrations decreased with increasing depth in the sediment cores collected.

Also as part of U.S. Navy-sponsored investigations, Grovhoug *et al.* (1986) compared water, sediment, and bivalve organotin concentrations in a number of U.S. harbors between 1984 and 1986 (Table 12.2). Sediment concentrations were reported for six sites around the nation sampled in 1984, including San Diego Harbor. In each area, three general site types were defined and analyzed: locations with moderate to extensive naval use, locations with high commercial and recreational use, and locations of special ecological value (for example, spawning beds or nursery grounds). Within San Diego Harbor, sediments from naval-use areas contained 0.087 ± 0.0523 ppm dw organotin; from commercial/recreational areas, 0.178 ± 0.200 ppm; and from "ecological" areas, 0.009 ± 0.020 ppm. Among those sites nationwide for which sediment results were reported, these San Diego Harbor values were high (Table 12.2).

Table 12.2. Organic tin concentrations in sediment samples from 1984-86, summarized for respective use areas. Values in ppm dw total organic solvent extractable tin. Source: Grovhoug *et al.* (1986).

Location	Naval Use Areas			Comm'l/Recr'l Use			Special Signif. Areas		
	n=	Mean	Sdev	n=	Mean	Sdev	n=	Mean	Sdev
San Diego, CA	25	0.087	0.052	16	0.178	0.200	19	0.009	0.020
Norfolk, VA	15	0.049	0.055	24	0.024	0.044	10	0.004	0.006
Little Creek, VA	7	0.011	0.010	5	0.010	0.009	6	0.001	0.001
Mare Is. Strait, CA	9	0.005	0.002	12	0.005	0.004	11	0.004	0.004
Pearl Harbor, HI	11	0.006	0.016	3	0	-	6	0	-
Honolulu, HI	-	-	-	7	0.154	0.244	1	0.075	-

In 1986, Stallard *et al.* (1987) measured butyltin concentrations in sediments collected at 31 stations in southern California (Table 12.3 and Figure 12.4--note units). Concentrations of total butyltin (the sum of mono-, di-, and tri-butyltin) in individual samples ranged from less than 0.0022 ppm dw in the Mission Bay bird sanctuary to 0.056 ppm dw at the Marina del Rey County dock. Other marina sites in southern (as well as northern and central) California were sampled as well, and generally reflected relatively higher concentrations of butyltins than did sites along the coast or those presumably exposed to lesser amounts of vessel traffic. However, even within the subset of marina sites, sediment total butyltin concentrations ranged over an order of magnitude. In this survey, MBT concentrations ranged from below detection (less than 0.0004 ppm dw) at several sites, to 0.023 ppm in sediments at the Marina del Rey County dock (Table 12.3). This range is comparable to that reported in 1979 samples by Seidel *et al.* (1980).

Table 12.3. Butyltin concentrations in sediments collected at sites in the Southern California Bight February to June 1986. Values in ppb dw of butyltin cation. *nd* = not detected (detection limits approximately 0.4 ppb for MBT; 0.25 ppb for DBT; 1.5 ppb for TBT), *tr* = trace. Source: Stallard *et al.* (1987).

| Location	Mono-	Di-	Tri-	Sum
Santa Barbara charter boat pier	14	15	9	38
Channel Islands Harbor	9	3	2	14
Ventura Harbor	2	8	*tr*	10
	5.4	2.5	nd	7.9
Marina del Rey county dock	23	27	6	56
Marina del Rey, near MDR Hotel	10	22	7.7	39
Redondo Beach King Harbor	6.3	3.6	3.9	13.8
Redondo Beach, near Portofino Inn	2.6	0.6	nd	3.2
Long Beach Marina	1.5	0.27	0.54	2.31
	0.74	0.37	0.23	1.34
Long Beach downtown	4.2	4.4	*tr*	8.6
Seal Beach Navy Harbor	1.9	0.51	0.23	2.64
Seal Beach, Peters Landing	1.8	1.2	1.2	4.2
		2.1	0.7	2.8
	1.2	0.83	0.45	2.48
Huntington Bay	0.63	0.5	nd	1.13
Balboa Yacht Basin, Newport Bay	0.37	1.7	nd	2.07
	1.7	0.9	nd	2.6
Rhine Channel, Newport Bay Shipyard	4.8	3.9	0.74	9.44
Rhine Channel, Lido Shipyard, Newport Bay	1.7	1.7	0.5	3.9
Bahia Corinthian Yacht Club, Newport Bay	3.4	2.2	1.2	6.8
	1.7	1.1	0.37	3.17
Dana Point East	1.8	1.8	0.9	4.5
Dana Point West	2.2	1.9	0.45	4.55
Dana Point Dock D	3.0	1.5	nd	4.5
Dana Point South	1.8	1.8	0.9	4.5
Oceanside Marina	1.8	1.4	0.48	3.68
Oceanside Marina, across from USCG	2.1	1.4	nd	3.5
Campland on the Bay, San Diego Harbor	0.36	0.07	nd	0.43
Quivera Basin, Islandia Dock, San Diego Harbor	1.2	0.81	0.29	2.3
UCSD Bird Sanctuary, Mission Bay	*tr*	4	nd	4
	tr	*tr*	*nd*	—
	nd	nd	*nd*	nd
	nd	nd	*nd*	nd
Shelter Island Boat Ramp, San Diego Harbor	0.66	1.1	0.79	2.55
SIO Nimitz Marine Facility	3.9	2.6	1.1	7.5
	4.9	3.2	1.5	9.6
Hilton Hotel Dock, San Diego Harbor	1.2	0.33	nd	1.53
San Diego Harbor, between Piers 12 and 13	0.1	nd	nd	0.1
Spanish Landing, San Diego Harbor	2.1	0.4	*tr*	2.5
Chula Vista small boat marina, San Diego Harbor	0.6	nd	*nd*	0.6
	1.4	nd	nd	1.4
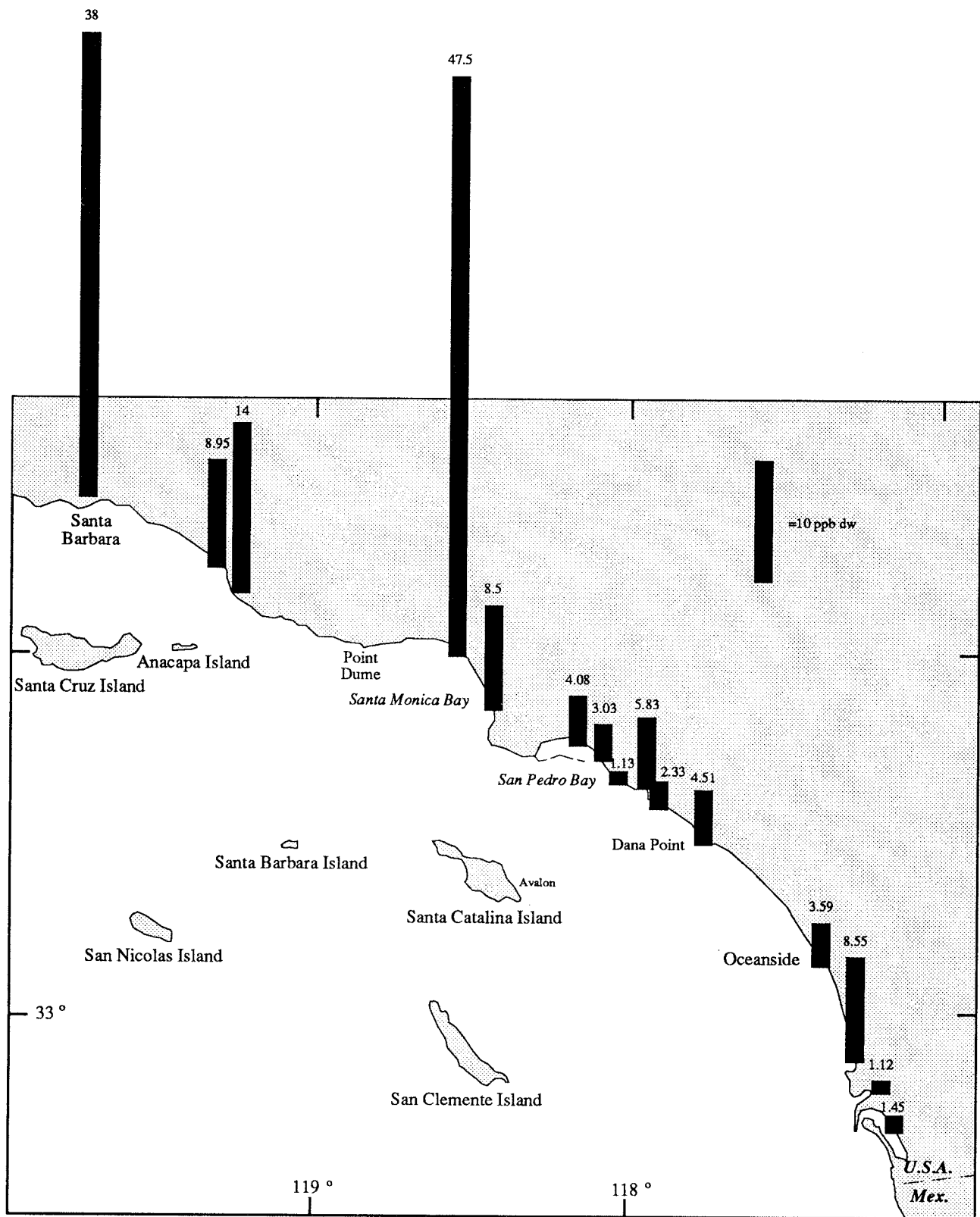
Figure 12.4. Mean concentrations (ppb dw) of total butyltin in sediments from 15 areas (including 36 sites) along the southern California coast in 1986. Plotted from Stallard et al. (1987) and data in Table 12.3.

The Mussel Watch Project of NOAA's NS&T Program undertook the measurement of butyltin concentrations in sediments collected at 33 sites around the coasts of the United States in 1987, with Texas A&M University performing the analyses (Wade *et al.*, 1988). Two southern California sites were included. While available results are preliminary in nature, they are notable here in that the highest total butyltin (the sum of mono-, di-, and tri-butyltin) concentration measured among the 33 sites was found in Los Angeles-Long Beach harbors (0.282 ppm dw). The TBT component of this total was reported to be 0.187 ppm dw, more than twice the next highest concentration that occurred at Chicopit Bay, St. Johns River, Florida (0.087 ppm dw). A second site, Harbor Island in San Diego Harbor, contained 0.060 ppm (total butyltin). The mean total butyltin and TBT concentrations for all 33 sites were 0.036 ± 0.056 ppm dw and 0.022 ± 0.035 ppm dw, respectively. Because of the large range and variability apparent in these results, median values may be more representative. For total butyltin, the median sediment concentration for the 33 sites was 0.012 ppm dw, while for the tributyltin fraction it was 0.010 ppm dw (NOAA, unpublished data).

In 1988, Stephenson *et al.* (1988) analyzed 105 sediment samples from the Shelter Island Commercial Basin in San Diego Harbor. Eighty-five samples collected in February 1988 contained a median TBT concentration of 1.2 ppm dw and a range of 0.7 to 13.0 ppm dw. Concentrations were less than 0.3 ppm dw in the center of the basin to more than 4.0 ppm dw near four major boat yards. Samples from a second collection (March 1988) confirmed that concentrations in unsieved sediments were directly proportional to the amount of paint chips in the sediment (large chips had concentrations ranging from 170 to 250 ppm dw). The authors suggested that deposited paint chips may continue to be sources of TBT to water and sediments long after cessation of TBT paints.

Although there do not appear to be any data for judging toxic concentations of TBT or other organotins in sediments, Cardwell and Meador (1989) applied an equilibrium partitioning approach to aquatic bioassay data that suggested a safe chronic TBT concentration about 0.14 ppm and a safe acute level of 1.59 ppm. Only sediments from some sites in the Shelter Island commercial basin in San Diego Harbor exceeded the acute level. Sediments from Shelter Island and several sites in Long Beach-Los Angeles harbors exceeded the chronic level.

There are no data on TBT in sediments from which to construct long-term time series. However, in San Diego Harbor, it appears the TBT levels in water of the Shelter Island Marina rose from below detection in 1978 (Hodge *et al.*, 1979), to below 0.1 ppb in 1983 and about 0.5 ppb in 1986 (Valkirs *et al.*, 1986). Since then, levels have apparently declined (Salazar, 1989).

TIN IN MUSSELS

Total Tin

Recognition that organotin vessel coatings are a potential threat has been a relatively recent phenomenon. As a result, large-scale programs of analysis for tin in southern California are not numerous; and nearly all of those available are for total tin, as opposed to individual species of inorganic and organic tin compounds.

The overall mean levels of total tin in mussels sampled by NOAA's NS&T Program between 1986 and 1989 was 0.189 ppm dw for *M. edulis* and 0.048 ppm dw for *M. californianus*. Median values were 0.131 ppm dw for *M. edulis* and below the detection limit for *M. californianus*.

In the 1974 SCCWRP survey, total tin was highest in digestive gland and gonad tissue and lowest in adductor muscle and all remaining tissue (Young *et al.*, 1975); thus, samples of whole tissue (such as measured in the NS&T Program) and whole tissue less gonad (such as measured in the CMW Program) will tend to produce lower concentrations than in digestive gland.

Fortunately, there is one early record of tin in mussels. The SCCWRP performed analyses of total tin in *M. edulis* digestive gland in 1974 as part of its study of three harbors (Young *et al.*, 1975). Results from these measurements are shown in Figures 12.5 to 12.7. Highest concentrations of total tin were found in the inner portion of Rhine Channel of Newport Bay (not shown--3.57 ± 1.90 ppm dw), at the northeast end of Shelter Island in San Diego Harbor (3.50 ± 0.98 ppm), and at the commercial docks in San Diego Harbor (3.25 ± 1.49 ppm). Considering these areas experienced heavy recreational, commercial, and military vessel traffic for decades, this distribution of elevated tin concentrations 15 years ago is not
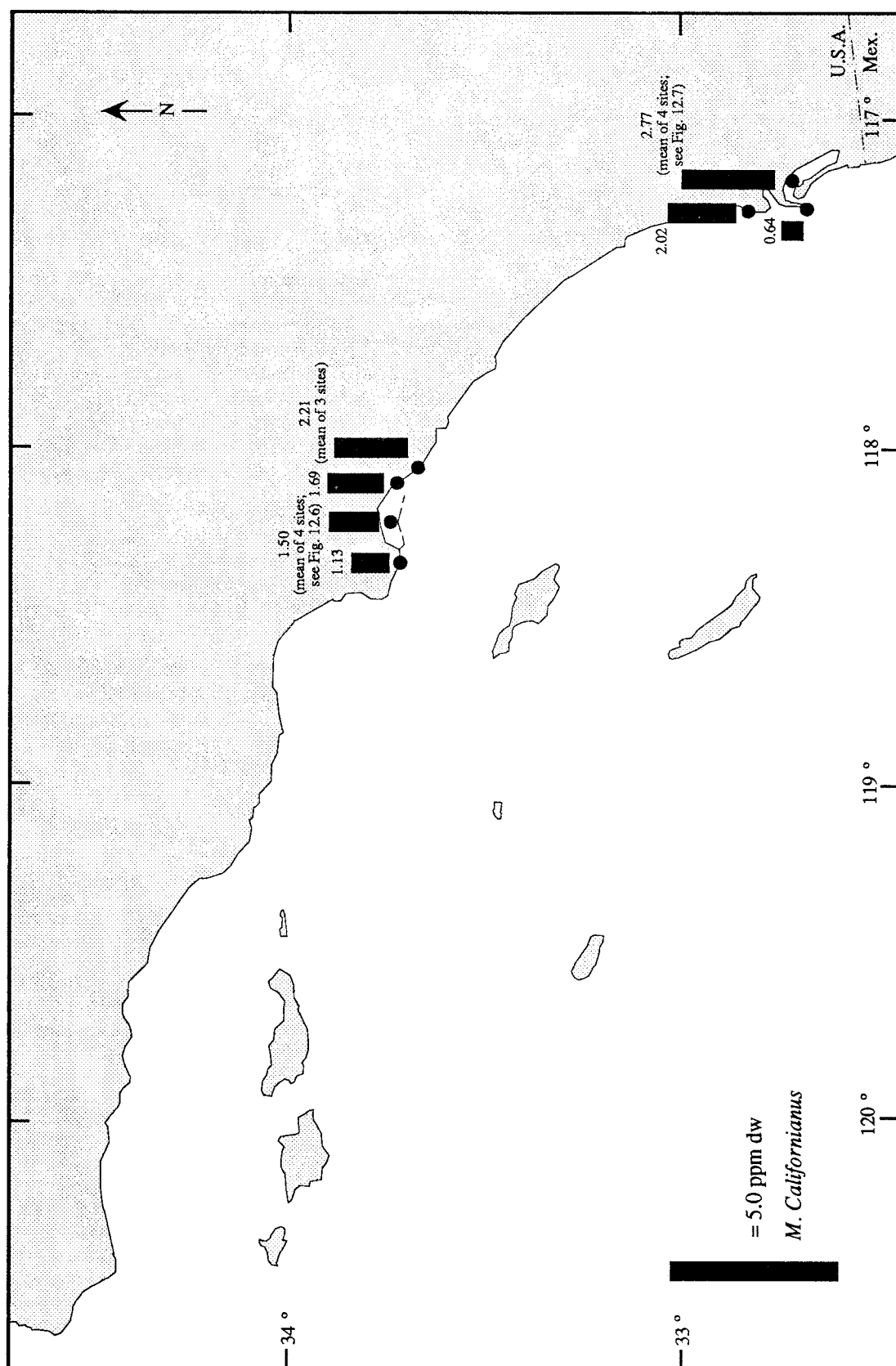
Figure 12.5. Total tin in digestive gland of mussels sampled in 1974. Source: Young et al., 1979; Young, unpublished.
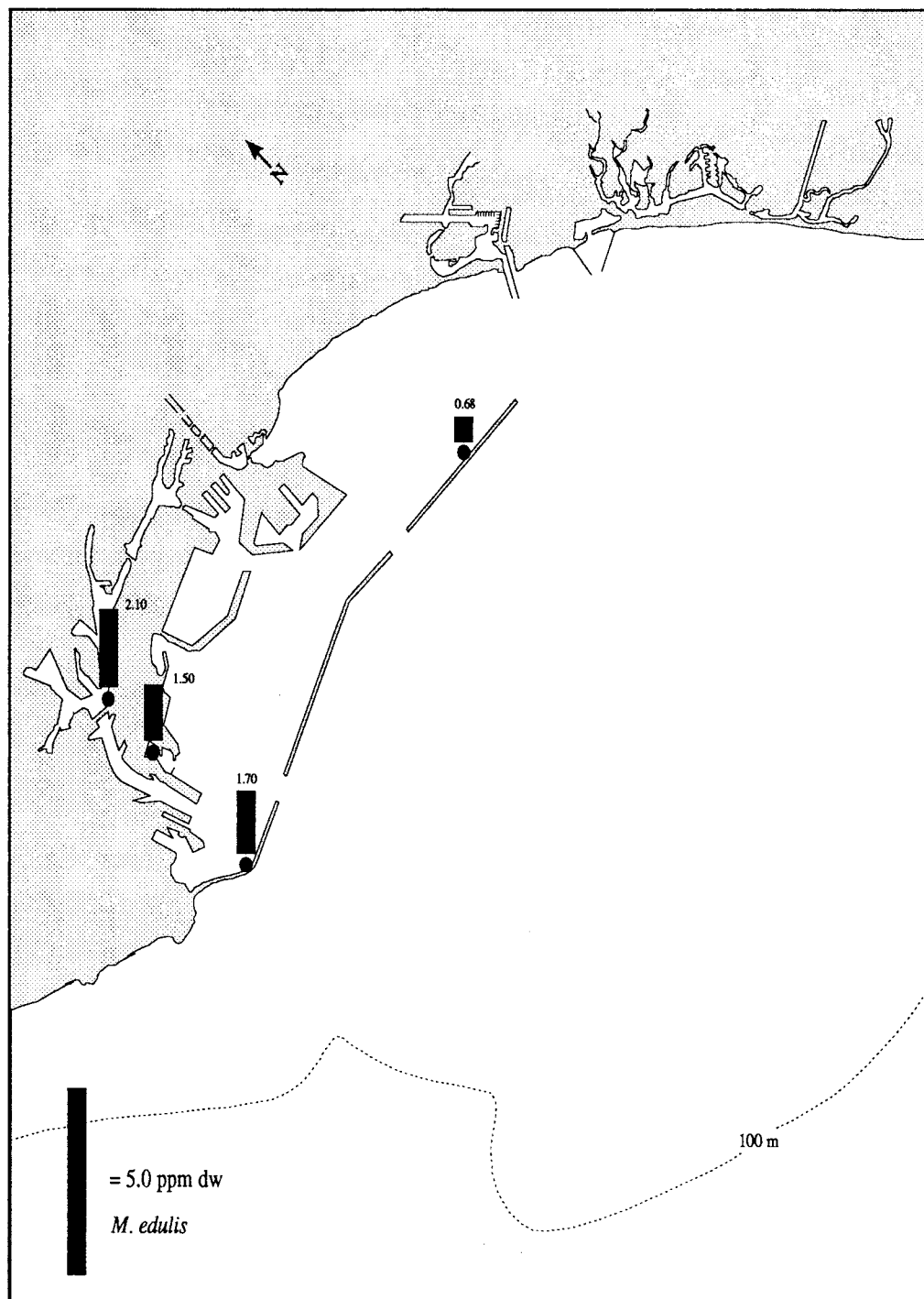
Figure 12.6. Total tin in digestive gland tissue of mussels sampled in San Pedro Bay in 1974. Source: Alexander et al., 1976; Young, unpublished data.
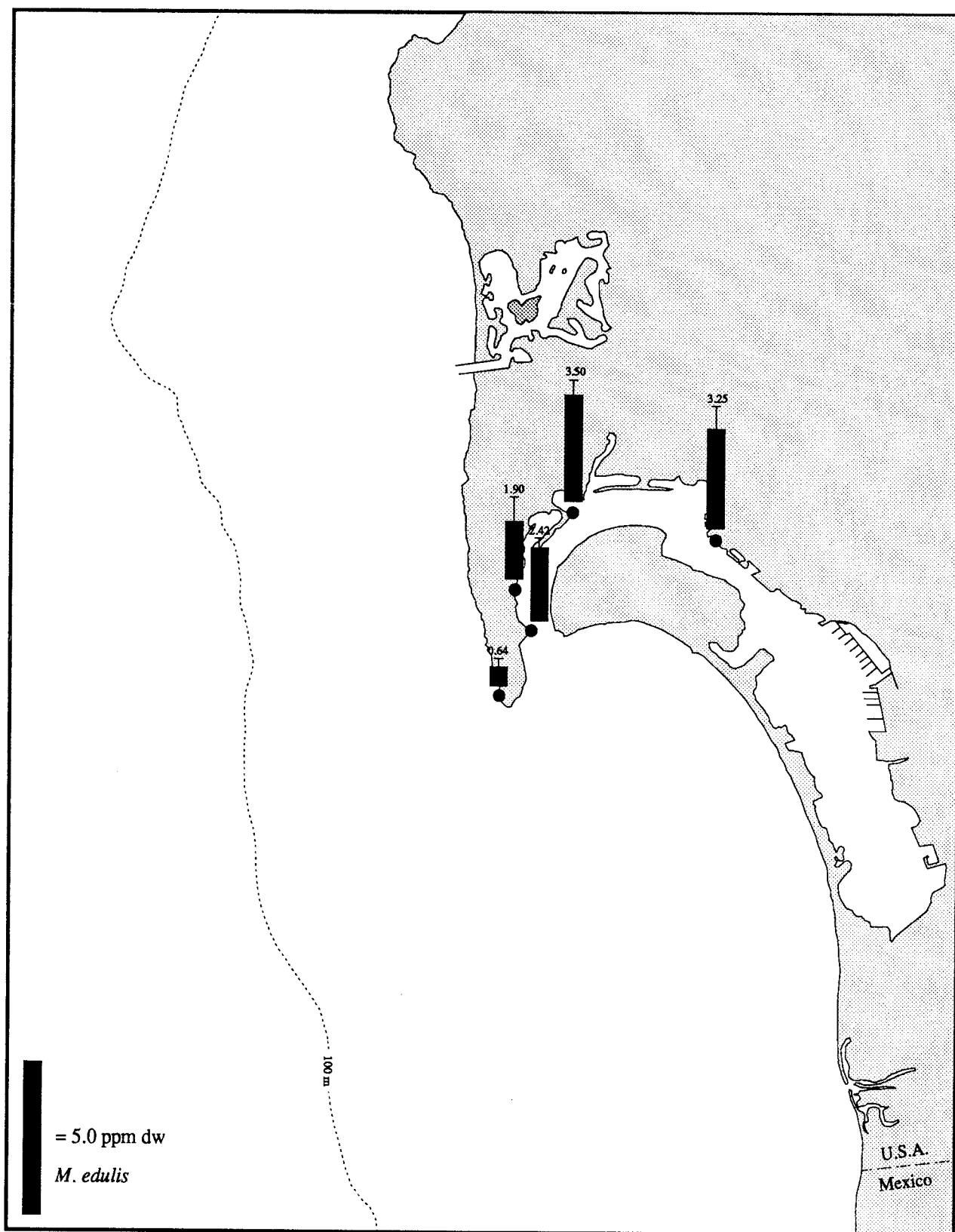
Figure 12.7. Total tin in digestive gland of mussels sampled in 1974. Source: Young et al., 1979.

surprising. The lowest digestive gland levels were found at Point Loma (0.64 ± 0.53 ppm), on the east breakwater of Long Beach Harbor (0.68 ppm), and at Royal Palms (1.13 ± 0.68 ppm). These sites represent relatively open, exposed areas not associated with shipping and boating activity. It is also notable that two of the three locations with lesser concentrations (Point Loma and Royal Palms) were sites in proximity to major municipal discharges. This suggests that municipal inputs were not a significant source of tin to nearby mussels.

Total tin (and butyltin) was measured in triplicate composites of whole mussels from up to 17 sites in southern California during NOAA's NS&T Program annual Mussel Watch surveys in 1986, 1987, and 1988. In 1986, all measurements at the 16 sites surveyed were below quantification limits ranging from 0.68 to 1.2 ppm dw (NOAA, 1989). In 1987, all measurements were again below quantification limits ranging from 0.9 to 0.95 ppm dw (NOAA, 1989). However, in 1988, average concentrations were well above the reduced quantification limits of 0.05 to 0.07 ppm, and, for the 17 sites surveyed, ranged from less than 0.057 ppm dw in *M. californianus* from a site on San Miguel Island to 3.8 ppm dw in *M. edulis* from a site on Harbor Island in northern San Diego Harbor (Table 12.4). The concentrations formed groupings generally related to distance from harbors and marinas. All samples from within harbors had high concentrations of total tin (2.4 to 3.8 ppm dw). In addition to the Harbor Island site, these concentrations included 3.57 ppm dw in *M. edulis* from the fish pier inside the Los Angeles Harbor breakwater near San Pedro and 2.43 ppm dw at the Ventura Bridge in Mission Bay. All mussel samples from the entrances to harbors had moderately high concentrations of total tin (0.4 to 1.0 ppm dw), including 1.08 ppm dw in *M. edulis* from the South Jetty at Marina del Rey, 0.68 ppm dw in *M. californianus* from the West Jetty at Alamitos Bay, 0.45 ppm dw in *M. californianus* at the Balboa Channel Jetty (entrance to Newport Bay), and 0.58 ppm dw in *M. edulis* at the Oceanside Beach Jetty. Samples of *M. californianus* from open coastal sites near urban areas or ocean outfalls had relatively low concentrations of total tin (0.1 to 0.4 ppm dw) including Point Santa Barbara (0.22 ppm dw), Point Dume (0.14 ppm dw), Royal Palms (0.36 ppm dw), and the Point Loma lighthouse (0.35 ppm dw). Finally, all but one of the whole mussel samples from island and coastal sites more distantly removed from urban centers and harbors had total tin concentrations at, near, or below the quantification limit (less than 0.06 to 0.09 ppm dw) including a site near the Imperial Beach fishing pier. The exception was a mean concentration of 0.12 ppm dw at Bird Rock near the Isthmus on the west end of Santa Catalina Island.

The overall mean levels of total tin in mussels sampled by NOAA's NS&T Program between 1986 and 1989 was 0.189 ppm dw for *M. edulis* and 0.048 ppm dw for *M. californianus*. Median values were 0.131 ppm dw for *M. edulis* and below the detection limit for *M. californianus*.

Although total tin has been measured by the CMW in some mussels on several occasions during the 1980s (Phillips, 1988), there are not enough data for constructing time series for any single location. Therefore, it is impossible to determine the direction or magnitude of long-term changes of tin concentrations in mussels anywhere in the Southern California Bight. Nonetheless, there is indirect evidence that total tin may have increased (or at least not decreased substantially) between 1974 and 1988 in mussels from harbors. As noted above, the 1974 SCCWRP harbor survey (Young *et al.*, 1975) sampled individual organs of mussels including digestive gland (data cited above). They also found that total tin concentrations were considerably higher in digestive gland and gonad than in adductor muscle or other remaining tissues. Thus, samples of whole mussels in 1974 would have produced lower concentrations of total tin than the values reported above for digestive gland from Newport Bay (3.57 ppm dw) and San Diego Harbor (3.5 and 3.25 ppm dw). As noted above, the 1988 whole mussel concentrations from sites within or near these sites were 0.58 ppm dw at the Newport Bay entrance and 3.8 ppm dw at Harbor Island in San Diego Harbor. Presumably, digestive gland concentrations in these 1988 mussels would have been considerably higher, and therefore equivalent to or higher than the levels reported by Young *et al.* (1975) from the 1974 collections. The first 3 years of the NS&T Mussel Watch Program (1986-88) showed no significant changes in tin in mussels from sites in southern California (NOAA, 1989).

Table 12.4. Mono-(M), di-(D), tri-(T), total butyltin (ΣBT), and total tin (ΣSn) concentrations as Sn mean in ppm dw, measured in mussels collected during NOAA's NS&T Program Mussel Watch Surveys in 1987 (Wade *et al.*, 1988) and 1988 (NOAA, unpublished data). Far right column is %ΣBT of ΣSn.

Site	Species	1987				1988				ΣSn	%ΣBT
		M	D	T	ΣBT	M	D	T	ΣBT		
Point Conception	c									0.094	
Point Santa Barbara	c									0.223	
San Miguel Island	c									<.057	
Santa Cruz Island	c									0.070	
Santa Catalina Island	c									0.117	
Point Dume	c									0.144	
Marina del Rey, South Jetty	e					0.006	0.160	0.246	0.411	1.083	37.95
Royal Palms	c					0.001	0.025	0.116	0.141	0.363	38.8
San Pedro fishing pier	e	0.74	0.52	1.54	2.80					3.567	(78.5)[1]
Alamitos Bay, West Jetty	c					0.004	0.083	0.304	0.392	0.680	57.65
Balboa Channel Jetty											
Newport Bay	c									0.453	
Oceanside, Beach Jetty	e									0.580	
Mission Bay Ventura Beach	e	0.29	0.26	0.68	1.23	0.042	0.433	0.777	1.252	2.43	51.5
Point Loma light	c					nd	0.007	0.091	0.099	0.353	28.05
Point La Jolla	c					nd	0.001	0.020	0.021	0.070	30.00
Harbor Island,											
San Diego Harbor	e	0.64	.083	0.91	2.38	0.212	0.866	1.337	2.414	3.80	63.53
Imperial Beach	c					nd	0.021	0.039	0.061	0.070	87.14

c = *Mytilus californianus*
e = *Mytilus edulis*
[1] 1987 butyltin as percent of 1988 total tin
nd = not detected

Organotin

Butyltin concentrations have been measured in mussels and other bivalve species in several recent synoptic surveys and, as a result, offer comparisons of local data at the national, regional, and local level. In addition, one recent (1988) NOAA NS&T survey offers a comparison of butyltin and total tin concentrations.

Grovhoug *et al.* (1986) collected and analyzed organotin concentrations in *M. edulis* between 1984 and 1986 from a number of locations in San Diego Harbor. As was true for sediment, results were grouped into three general site types: those with relatively high naval traffic, those in commercial and recreational use areas, and those in ecologically important areas. In naval use regions, mussel tissue concentrations of total butyltins were 1.50 ± 0.58 ppm dw; in commercial/recreational regions, 2.69 ± 1.34 ppm; and in ecologically significant regions, 0.93 ± 0.44 ppm.

TBT accounted for about half the total butyltin concentrations in the 1987 samples from southern California and were 0.91 ppm at Harbor Island in San Diego Harbor, 0.68 ppm at Mission Bay, and 1.54 ppm at the San Pedro Bay fishing pier (Wade *et al.*, 1988; Table 12.4). From samples collected at three San Diego Harbor sites in October 1986, Short and Sharp (1980) reported concentrations ranging from 0.19 to 0.44 ppm ww, as TBT. On a dry weight basis (approximately 5 times higher than wet weight levels) these may have been higher than the values reported by Wade *et al.* (1988).

In 1987, the NS&T Mussel Watch analyses included measurements of tri-, di-, and mono-butyltin concentrations in bivalve (either *M. edulis*, *C. virginica*, or *O. sandvicensis*) tissue at 36 sites along the nation's coasts (Wade *et al.*, 1988). *M. edulis* were collected at 14 of the 36 sites, including 3 sites in

southern California--San Pedro Bay, Mission Bay, and San Diego Harbor. Limiting the discussion here to the 14 *M. edulis* sites located along the Pacific and northeast Atlantic coasts, total butyltin concentrations in mussels from the three southern California locations represented three of the four highest concentrations measured. The highest *M. edulis* value nationwide was 2.82 ppm dw (near a marina in northern Puget Sound). The three southern California sites were: San Diego Harbor Island, 2.38 ppm dw; Mission Bay Ventura Bridge, 1.23 ppm dw; and San Pedro Bay breakwater fishing pier, 2.8 ppm dw (Table 12.4). The mean for the three southern California sites was 2.14 ppm. By contrast, the mean for the remaining 10 sites was 0.32 ppm.

In 1988, the NOAA NS&T Program measured butyltins in mussels from eight southern California sites between Marina del Rey and Imperial Beach. Total butyltin concentrations ranged from 0.021 ppm dw in *M. californianus* from Point La Jolla to 2.41 ppm dw in *M. edulis* from Harbor Island in San Diego Harbor (Table 12.4). Like total tin, reviewed above, concentrations of butyltins were highest at or near entrances to harbors (0.39 to 2.41 ppm dw, including Marina del Rey, Alamitos Bay, Mission Bay, and San Diego's Harbor Island), intermediate at open coastal sites near urban areas (0.10 ppm dw at Point Loma and 0.14 ppm dw at Royal Palms), and low at more distant sites (0.02 ppm dw at La Jolla and 0.06 ppm dw at Imperial Beach; Table 12.4).

As noted above, the 1988 NOAA NS&T survey also included measurements of total tin (Table 12.4). For the eight sites surveyed in 1988 that included measurements both of butyltins and total tin, the sum of butyltins accounted for 28 to 87 percent of the total tin (Table 12.4). There was no apparent pattern of the composition of tins by site or overall concentrations except (possibly) that when each species is examined separately there was a tendency for the butyltin fraction to increase with increasing total tin concentration. However, samples from Imperial Beach, which had low butyl and total tin concentration, had a high fraction of tin as butyltin (87%) and therefore deviated strongly from this pattern.

Comparing measured concentrations of butyltins in mussels to those in nearby sediments (Texas A&M University performed both sets of analyses) through the nonparametric Spearmans rank correlation statistic indicates that there is no significant correlation (at p = 0.1) between mussel butyltin and sediment butyltin (r_s = 0.35, at a significance level of 0.246). For example, although the Los Angeles-Long Beach harbors site yielded comparatively high concentrations of total butyltins in mussels (2.80 ppm) and sediment (0.28 ppm), the highest *M. edulis* concentration in Bellingham Bay, Washington, was paired with a relatively low sediment value of 0.01 ppm at the same site.

TIN IN FISH AND OTHER SPECIES

Seaweeds have been measured for Sn IV from the Scripps Pier, La Jolla (Hodge *et al.*, 1979) and from 11 sites in San Diego Bay and San Diego Harbor (Seidel *et al*, 1980). Concentrations ranged from 0.015 ppm dw in a sample of the green algae, *Enteromorpha* from Buoy 19 near the entrance of the harbor to 1.29 ppm dw in a sample of *Sargassum* taken at the nearby U.S. Navy anti-submarine warfare dock. Highest median concentrations were in *Sargassum* (1.11 ppm dw), sea lettuce (*Ulva*; 0.51 ppm dw), and *Egregia* (0.39 ppm dw). Concentrations in giant kelp, *Macrocystis pyrifera*, ranged from 0.06 ppm dw at a mid-bay site (Seidel *et al.*, 1980) to 0.83 ppm dw at the Scripps Pier at La Jolla (Hodge *et al.*, 1979). There was no obvious gradient of increasing contamination toward the head of the bay; however, it is curious to note that the highest median or single concentration of tin was in seaweeds from the Scripps Pier site.

Total tin in two invertebrate species measured by Hodge *et al.* (1979) from San Diego Bay sites were 0.014 ppm dw in *Aglaophenia* spp. and 0.054 ppm dw in *Bugula* spp.

Very limited information exists for concentrations of tin in fish collected in the Southern California Bight. As part of the nationwide 1971-77 Microconstituents Program (Hall *et al.*, 1978), total tin was measured in muscle, liver, or whole tissue of a variety of fish and macroinvertebrates from the Southern California Bight. The range of average tin concentration was 0.4 to 0.6 ppm ww for both muscle and liver, and 2.0 to 4.0 ppm ww for whole fish. No individual values were below 0.15 ppm ww (Hall *et al.*, 1978). All these values are markedly higher than concentrations reported by other investigators as described below.

In 1979, SCCWRP sampled fish species in Los Angeles Harbor and analyzed muscle tissue for concentrations of selected contaminants, including tin. These results are listed in Table 12.5. Relative to the tin measurements in digestive glands of resident Los Angeles-Long Beach mussels made by SCCWRP in 1974, the concentrations in fish muscle were lower by an order of magnitude.

Table 12.5. Tin in single muscle tissue composites of three fish species collected in Los Angeles Harbor in 1979. Source: Young, unpublished data.

Species	Number in composite	Tin, ppm ww	Tin, ppm dw
Anchovy (*Engraulis mordax*)	65	0.016	0.064
White Croaker (*Genyonemus lineatus*)	24	0.048	0.222
Halibut (*Paralichthys californicus*)	16	0.043	0.202

The NS&T Benthic Surveillance Project analyzed total tin concentrations in livers of three southern California fish species in 1984 (Figure 12.8). The minimum southern California concentration was measured in hornyhead turbot collected at Dana Point (0.01 ± 0.001 ppm ww) and the maximum in barred sand bass from San Diego Harbor (0.49 ± 0.46 ppm ww). Among trace metals reviewed in this report, these data are unique. For most trace metals, concentrations in livers of fish from urban and rural sites were similar or *lower* in the more contaminated urban areas such as San Pedro Canyon, Seal Beach, or San Diego Harbor. Tin appears to be different in these fish, behaving more like PCBs or DDT, in that concentrations in all three NS&T species were generally higher in fish from the urban or harbor sites. Tin in fish liver is also lower than in mussel digestive glands sampled in 1974.
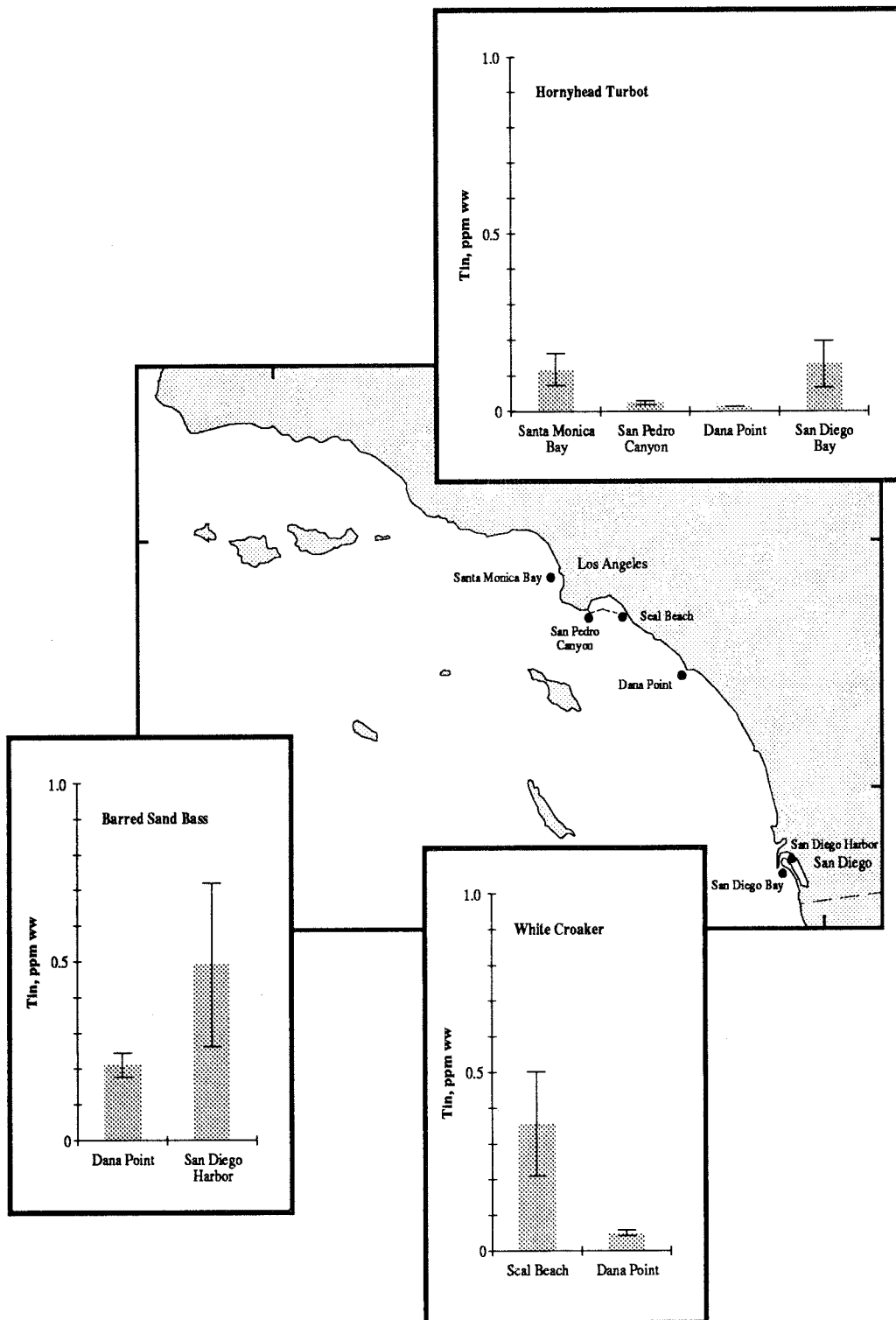
Figure 12.8. Concentrations of total tin measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

To our knowledge, no data are yet available concerning concentrations of organotins in fish or macroinvertebrates from the Southern California Bight. For future reference, it is noted that Sullivan *et al.* (1988) found butyltin concentrations in salmon from Puget Sound to be less than 0.005 to 0.007 ppm ww in returning ocean fish, 0.011 to 0.030 ppm ww in resident blackmouth, and 0.057 to 0.188 ppm in pen-reared fish. There is little evidence that tin may undergo biomagnification in food webs (Table 12.6).

Table 12.6. Summary of concentration ranges of total/inorganic tin in various samples from the Southern California Bight. Based on data reviewed in text.

Type of sample	lowest	highest	sample condition and units
Sediments	0.07	89.0	ppm dw
Mussels, whole	0.057	3.8	ppm dw
digestive gland	0.64	3.57	ppm dw
Seaweeds	0.015	1.29	ppm dw (Sn IV)
[1] Invertebrates	0.014	0.054	ppm dw (Sn IV)
[1] Fish, muscle	0.016	0.048	ppm ww
	0.06*	0.19*	ppm dw, estimated
liver	0.01	0.49	ppm ww
	0.04*	2.0*	ppm dw, estimated

[1] Excluding data in Hall *et al.*, 1978, which ranged from 0.4 to 0.6 ppm ww for muscle and liver and 2.0 to 4.0 ppm ww for whole animals.

* Estimated concentrations using 20 percent dry weight.

There are no U.S. action limits or criteria for tin or organotins in seafood. Based on data in Nauen (1983), 12 nations have criteria or limits that range from 50 to 250 ppm ww, with a median of 175 ppm ww. These limits were presumably set to protect consumers from contamination by tin from canning. No concentrations measured to date in mussels or fish from the Southern California Bight approach the minimum of 50 ppm. However, sampling is inadequate to determine the range in popular fish and other seafood organisms.

SUMMARY AND CONCLUSIONS

There are no measures or firm estimates of tin or organotin inputs to the Southern California Bight. Extrapolations from various data suggest tin inputs through sewage might be approximately 3 to 6 mt per year (as Sn IV) while TBT from vessels might have been (before legislation) some fraction of 157 mt per year for the Pacific Coast.

Vessel paint scrapings are known to contain total tin concentrations in the range of 360 to 2400 ppm dw. Total tin concentrations in sediments ranged from 1 to 89 ppm dw, with lowest concentrations on the mainland shelf and highest in harbors, mainly San Diego Harbor. By contrast, organic (butyl) tin concentrations in sediments ranged no higher than 0.3 ppm dw and at most harbor sites were below 0.01 ppm dw except in Marina del Rey, Santa Barbara Harbor, Channel Islands Harbor (Oxnard), and King Harbor (Redondo).

Total tin concentrations in digestive glands of mussels were 2 to 5 times higher in harbors than outside harbors in 1974. Average butyltin concentrations were nearly 10 times higher in mussels from three southern California harbors (2.14 ppm dw) than in ten other U.S. harbors (0.32 ppm dw). Concentrations of TBT in water from one of the most contaminated areas, Shelter Island Marina in San Diego Harbor, appear to have increased rapidly (to well within toxic concentrations) between 1983 and 1986, but have

apparently declined since then, possibly in response to controls implemented in 1988. There appears to be no relation between butyltin in mussels and butyltins in adjacent sediments. Total tin was higher in liver of fish from urban and harbor sites than in comparable specimens from a coastal control site, the only metal to produce such a pattern. No data was found on organotin levels in fish from southern California.

There is evidence that, unlike other trace elements, tin has accumulated in livers of flatfish from harbor areas known to be contaminated with tins. No other trace element behaves this way in fish from the Southern California Bight. As noted in the text above, data from Davies and McKie (1987) indicate that total tin in livers can increase more than an order of magnitude in fish exposed to TBT. Thus, it is possible that flatfish from sites such as San Diego Harbor and Los Angeles-Long Beach harbors have experienced elevated tin concentrations as a result of exposure to TBT or other butyltin compounds in sediments, food, or water. It is not known if TBT is responsible for these higher levels of total tin because butyltin has not been measured in local fish. It is also possible, based on data from Seidel et al. (1980), that seaweeds may accumulate tin upon exposure to organotin compounds. Tin concentrations in resident organisms from the Bight are several orders of magnitude below published international seafood criteria.

INFORMATION NEEDS

As a result of recent legislation, use of organotin paints is sharply limited from what it was a few years ago. However, it is still not at all clear how vessel utilization and inputs compare to other sources for both total tin and organotins. Such knowledge, if available, would put current legislation in a useful perspective.

The long-term regional history of inputs of tin (and perhaps, organotin) could be determined by analyses of tins in dated sediment cores from nearshore basins and some harbors. Inputs of total and organic tin from sewage and run-off should be measured and compared with inputs from vessels. The global increase in atmospheric tin from sewage incineration suggests the possibility of a significant aerial source of tin (and perhaps some organotins) around major cities that combust sludges, so that aerial deposition and run-off may be worth measuring.

The possibility exists that the apparently elevated (ppm) concentrations of total tin in sediments, mussels, and livers of fish from harbor areas of the Southern California Bight, are results of long-term accumulations of organotin compounds (tin may be a metabolic residual). Contaminated sediments may continue to remain contaminated despite major reductions of inputs. Both total tin and organotins (especially butyltin) should be measured in sediment, mussels, and fish close to and away from potential sources. Experiments should be conducted to determine if long-term exposure of fish or shellfish to butyltin compounds and tin-contaminated sediments results in large accumulations of total tin regardless of the form.

The toxicity of tin and TBT (or other organotins) in sediments is unknown. Data may be needed to help judge the potential effects of sediments that contain paint chips.

The units in which tin and organotins were reported were not uniform, requiring great caution when comparing data. Uniform procedures should be adopted for reporting on the basis of molecular reference (as Sn IV or TBT), sample condition (dry or wet), and absolute units (ppb, ppm). The same care is needed in promulgating criteria and standards.

The lack of any data on concentrations of organotins in fish or other popular seafood species in southern California is surprising. Measurements should be made so that benefits of legislation and enforcement of criteria might have some chance of being realized.

Finally, with the possible exception of a site in Shelter Island Marina, San Diego, there does not appear to be in place, nor has there been, any kind of repeated monitoring program to track local, regional, near-term, and long-term trends of tin and organotin concentrations in sediments, fish, or shellfish. Such data are needed to track the progress of already implemented controls. Recently sampled sites and substrates are good candidates for continued re-occupation and sampling. Such monitoring should also include a biological effects component and measurements of any materials that will be used to replace the recently controlled organotin compounds. These include copper; which has, and continues to be, at toxic levels in some marinas (Salazar, 1989).

CHAPTER 13

ZINC

Zinc is ubiquitous in the environment, has many industrial uses, and is a biologically essential micronutrient. A major application of zinc is in galvanization, the coating of other metals to protect against corrosion. Zinc is also widely used as a component in batteries and vehicle tires. Sources to the marine environment include municipal wastes, direct industrial discharges, surface run-off, atmospheric fallout, barged wastes, and corrosion protection devices for boats and ships (Young et al., 1980).

More than 70 metalloenzymes require zinc as a co-factor, and as a result, zinc deficiencies can affect health in a number of ways (Goyer, 1986). Toxic effects from zinc, on the other hand, are relatively uncommon and require high levels of exposure. Dietary zinc concentrations 100 times greater than normal requirements have been administered to experimental animals with no apparent adverse effects (Goyer et al., 1979). Zinc is incorporated into tissues of zooplankton that may result in recycling in oceanic surface waters for many years (Reinfelder and Fisher, 1991). However, in the aquatic environment, zinc is known to be toxic if introduced at high enough concentrations (Young, Jan, and Hershelman, 1980). Akberali et al. (1985) found that zinc in solution inhibited cellular respiration in sperm and eggs of M. edulis.

Although zinc accumulates readily in bivalve mollusk species (with concentration factors from ambient seawater ranging from 1525 to 4 million), uptake in natural populations is mediated by a number of factors, including season, location, size, substrate, sex, and other considerations. Proximity to anthropogenic point sources appears to be one of the more important variables in determining zinc body burdens (Eisler, 1981).

Zinc is an important material in rubber tires and is present in percent concentrations (Christensen and Guinn, 1979). Thus, like lead, the high automobile activity in the Los Angeles, Orange County, and San Diego basins may lead to high levels of zinc in surface run-off and significant aerial inputs to the Bight. Several input and flux studies reviewed below seem to support this possibility in southern California.

In 1971, approximately 4200 mt of zinc entered the Southern California Bight from non-advective inputs (SCCWRP, 1973). Of this, 52 percent (2260 mt) entered from direct rainfall, 40 percent (1680 mt) from wastewater discharges, 4 percent (164 mt) from vessel coatings (paints, primers), 2.4 percent (101 mt) from surface run-off, and 1 percent from ocean dumping. A more recent budget does not exist. However, for the water year 1978-79, Young et al. (1981) estimated that the mass emission of zinc to the Los Angeles coastline from sewage and run-off was 930 mt. Of this total, run-off accounted for about one third (330 mt). In one 1986 storm, the Los Angeles River discharged 7.9 mt of zinc into coastal waters off Long Beach, a rate 10 times higher than for sewage inputs over the same several-day period (SCCWRP, 1987a). Zinc inputs from municipal sewage discharges continued to decline to 377 mt in 1985 (Figure 13.1), and to 250 mt in 1987 (about 13% of the 1971 input). Therefore, run-off may now be the dominant source of zinc to the Bight (Figure 13.1). In a review of data from basin sediment cores around the Bight, Bertine and Goldberg (1977) found that zinc fluxes decreased as the square of the distance from the Los Angeles area, supporting their conclusion that the major transport mechanism of anthropogenic zinc to the Bight was atmospheric and not via ocean currents from wastewater outfalls.
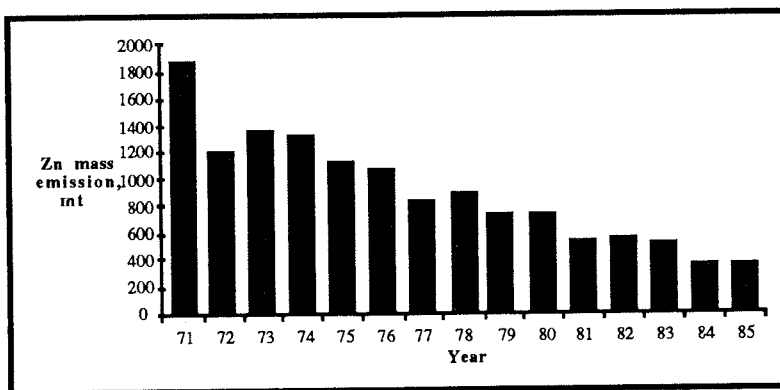

Figure 13.1. Combined annual mass emissions of zinc for seven southern California municipal wastewater dischargers, 1971-85. Source: SCCWRP, 1986.

Zinc fluxes from direct aerial fallout to local coastal waters increased 5- to 6-fold during a major (65,000-acre) brushfire in 1975 (Young and Jan, 1977). When compared to prevailing sewage inputs at that time (1100 mt per year), the extrapolated annual brushfire input was minor (260 mt). However, sewage emissions have now been reduced to rates comparable to what might occur from direct atmospheric fallout. Thus, brushfires should no longer be excluded as important sources, either as direct aerial fallout or indirectly through run-off.

Among the common trace elements reviewed in this report, zinc has been subject to an unusual and unique research and monitoring history, due largely to surveillance of the fate of radioactive [65]Zn. During the 1950s and early 1960s, [65]Zn was released to the atmosphere from nuclear bomb tests in the Pacific and into the California Current system from the Columbia River as a result of discharges from the Hanford Nuclear Reservation in the State of Washington. Test ban treaties resulted in cessation of atmospheric testing in the mid 1960s. "Mussel watch" surveys in 1963-64 and 1971 (Young and Folsom, 1973) yielded a [65]Zn "ecological" halflife in southern California mussels of 250 days. Hodge et al. (1973) reported a tenfold decrease of [65]Zn in livers of southern California albacore tuna between 1964 and 1971 and suggested that the decline would have been greater in the absence of Chinese nuclear weapons testing which began in 1967. While the radioactivity of [65]Zn makes its toxicological consequences quite different from those of stable zinc, the radio-ecology surveys nevertheless provide important data about the cycling of this element in large-scale ecosystems such as the Southern California Bight.

ZINC IN SEDIMENT

Zinc has been analyzed in hundreds of sediment samples from the Southern California Bight. Concentrations identified from selected data sets (Table 13.1) ranged from 4.2 ppm dw in the mouth of the Tijuana estuary in 1988 (Gersberg et al., 1989) to 13,700 ppm dw near a Newport Bay shipyard sampled in 1972 (as cited in Young et al., 1975).

Zinc is a natural component in crustal materials present at 65-80 ppm dw (Hodgson, 1963). Mean "reference" or "background" zinc concentrations in surface sediments along the 60-m isobath from rural coastal shelf areas have ranged from 40 ppm dw along the coast between Port Hueneme and Point Dume (Ventura/Los Angeles counties) in 1977 to 72 ppm dw along the coast between Newport and Dana Point sampled in 1985 (Table 13.1). Katz and Kaplan (1981) computed a reference mean of 44.4 ppm dw from the 60-m survey data, a mean of 108 ppm dw for deep cores from all areas, and a mean of 57 to 80 ppm dw for the bottom of cores near outfalls.

The overall mean value of zinc in sediment from all sites measured by NOAA's NS&T Program between 1984 and 1989 is more than twice the background level calculated by Katz and Kaplan (1981). The overall mean zinc concentration for NS&T sites is 93.808 ppm dw (median, 77.583 ppm dw).

Sediment zinc concentrations in areas remote from point sources are highly dependent on depth-related characteristics. Along the coast between Point Dume and Port Hueneme, Hershelman et al. (1982) found zinc concentrations were significantly (p <0.001) related to organic content (% total volatile solids, $r^2 =$ 0.932), amount of fine-grained sediment (% <63 μm, $r^2 = 0.892$), increasing water depth (10 to 700m, $r^2 = 0.805$), and inversely to solids content ($r^2 = -0.942$). Similar but slightly weaker correlations were found for the San Pedro Basin shelf (Thompson et al., 1986). In general, concentrations increased from about 10 to 20 ppm dw inshore to over 90 ppm dw offshore.

The estimate of what constitutes background or reference concentrations for zinc depends not only on depth, but also on the strength of reagents used to extract zinc from sediments. In a box core taken before 1974 at a depth of 75m off Whites Point, Palos Verdes, Bruland et al. (1974) obtained a total zinc concentration of 1800 ppm dw divided into sequential extraction fractions as follows: 1530 ppm (85%) reducible (by acetic acid in hydroxylamine hydrochloride), 144 ppm (8%) oxidizable (by 30% hydrogen peroxide), and 126 ppm (7%) resistant residue. By contrast, zinc in sediments from several basins was mainly in the resistant form (74 to 77%) with only small fractions in the oxidizable (9 to 18%) and reducible (14 to 18%) forms. An implication is that the excess zinc in Whites Point sediments may have been available for bioaccumulation in benthic organisms. Katz and Kaplan (1981) estimated, from shelf samples collected by Chow and Earl (1979), that the mean coastal shelf "leachable" (by weak acid extraction) zinc concentration was 11.8 ppm dw; whereas, the mean "total" (by strong acid extraction) zinc was 53.7 ppm dw. Katz and Kaplan (1981) also concluded that zinc and several other trace element concentrations in the rural areas described were unaffected by municipal wastewater discharges and the overall shelf background reference concentrations were about 10 to 50 ppm dw. Results of various studies may therefore not be directly comparable due to the strength of acids used to extract zinc.

Table 13.1. Mean, median, minimum, and maximum zinc concentrations in surface sediment from selected surveys, 1970-85 in ppm dw.

Site	Year	N	Mean	Median	Minimum	Maximum	Standard Deviation	Source
Rural Coastal Shelf (60 meters only):								
Santa Barbara shelf	1977	11	51	38	23	110	27	1
	1985	4	47	47	45	48	1	2
Port Hueneme to Point Dume	1977	4	40	41	36	44	3	1
	1980	11	46	46	32	71	11	3
	1985	2	53		48	58	7	2
Newport to Dana Point	1977	3	50	48	44	59	8	1
	1978	6	62	66	42	73	11	4
	1985	1	72					2
Outfall Areas:								
Oxnard shelf	1971[a]	4	53	50	37	76	16	9
Santa Monica Bay	1970[a]	24	90	86	58	160	26	9
	1977[b]	13	78	66	52	143	28	1
	1978[b]	31	93	83	42	265	45	4
	1985[b]	3	34	35	27	40	7	5
Palos Verdes shelf	1970[a]	22	472	380	79	1800	379	9
	1974[b]	7	1882	1610	598	2790	807	6
	1977[b]	8	661	510	37	2096	700	1
	1978[b]	8	572	515	77	1006	325	4
	1980[b]	7	776	629	240	1150	351	6
	1985[b]	10	488	445	123	985	308	5
	1985[b]	7	593	506	214	985	306	6
	1988[b]	7	346	252	78	656	233	6
Orange County shelf	1970[a]	13	95	96	57	150	25	9
	1977[b]	11	50	47	36	88	14	1
	1978[b]	12	56	58	26	67	11	4
	1985[b]	9	59	54	44	112	21	7
Point Loma shelf	1970[a]	5	63	59	53	83	12	9
	1977[b]	7	57	42	10	172	53	1
	1985[b]	8	51	46	35	93	18	8
Bays and Harbors:								
Marina del Rey[a]	1977	11	228	218	32	449	119	10
	1978	11	151	152	69	274	61	10
	1984	12	268	229	170	469	96	11
	1985	12	245	192	42	490	139	12
	1987	13	254	215	25	660	160	13
Los Angeles-Long Beach harbors [a]	1973	31	188	176	14	501	106	14
	1978	31	253	184	67	1317	231	15
Bolsa Bay	1979-80	6	38	31	24	82		20
Upper Newport Bay[a]	1980	8	105	113	54	135	26	16
Upper Newport Bay	1971	3	78	104	5	124	64	18
Lower Newport Bay	1971	7	188	147	59	410	118	18
Newport shipyards	1972	9	3376	847	246	13700	4441	19
	1981	9	432	410	224	810	195	19
	1986	6	264	295	150	370	84	19

Table 13.1 (continued)

Site	Year	N	Means	Median	Minimum	Maximum	Standard Deviation	Source
San Diego Harbor[a]	1983	20	500	273	43	4300	924	17
San Diego Harbor	1974	11	404	365	270	626	126	18
Tijuana estuary, mouth	1988	5	6.4	5.7	4.2	10.3	2.4	21
Tijuana estuary, north arm	1988	14	18.2	10.0	4.6	89.7	22.7	21
Tijuana estuary, south arm	1988	26	29.7	50.1	5.3	140	48.2	21
Tijuana estuary, river	1988	10	86.7	75.6	20.9	204	54.4	21
OVERALL		**419**				**13,700**		

[a] - all depths; [b] - 60-m only

1 Word and Mearns, 1979	8 City of San Diego, original data,	15 Soule and Oguri, 1980a
2 Thompson *et al.*, 1987	9 SCCWRP, 1973; Galloway, 1972	16 MBC and SCCWRP,1980
3. Hershelman *et al.*, 1982	10 Soule and Oguri, 1980b	17 Ladd *et al.*, 1984
4 Hershelman *et al.*, 1980	11 Soule and Oguri, 1985	18 Young *et al.*, 1975
5 Hyperion Treatment Plant, original data,	12 Soule and Oguri, 1986	19 Liu and Schneider, 1988
6 CSDLAC, original data	13 Soule and Oguri, 1987	20 Feldmeth, 1980
7 CSDOC, original data	14 Chen and Lu, 1974	21 Gersberg *et al.*, 1989

Assuming a "background" of 44 ppm dw (Katz and Kaplan, 1981), zinc concentrations in surface sediments (extracted with strong acid) near major sewage discharge areas have been elevated above background by factors varying from 1.1 to 1.4 for the Oxnard, Orange County, and Point Loma discharge areas to mean area elevations of 8.1 to 43 at Palos Verdes (346 to 1882 ppm dw; Tables 13.1 and 13.2). Comparable surveys from Santa Monica Bay (for 1977 and 1978) yielded mean concentrations of 78 ppm dw (1977) and 93 ppm dw, an increase over background levels of 1.6 and 1.9 times, respectively. The most recent data (1985) indicate very low zinc values in Santa Monica Bay (35 ppm or 0.8 times background levels).

Unfortunately, there are no explicit background or reference values published for zinc in sediments of harbors, enclosed bays, or lagoons. Assuming that the "coastal" reference or background value of 44 ppm dw applies, then sediments in four of six harbor/bay areas reviewed here have been found to be considerably more contaminated with zinc than all coastal shelf wastewater discharge sites, except Palos Verdes. For example, the median zinc concentration from nearshore sites sampled in San Diego Harbor in 1983 was 6.2 times above "coastal background" or 273 ppm dw (range, 43 to 4300). This is similar to the 60-m 1985 Palos Verdes medians of 445 and 506 ppm dw (overall range, 123 to 985; Table 13.1) that have since declined to 252 ppm dw by 1988 (Table 13.1). Areawide median concentrations of zinc in sediments from Los Angeles-Long Beach harbors and in Marina del Rey in 1978 were comparable (184 and 152 ppm dw) and about 4 times the coastal background (Table 13.2). Levels in Marina del Rey may be influenced by high levels of zinc near to and in the mouth of Ballona Creek. The least contaminated bay in the Los Angeles-Orange County area was Bolsa Bay, with a 1980 median of 31 ppm dw. In the undeveloped Tijuana estuary, zinc concentrations increased landward, from a median of 5.7 ppm dw at the mouth, to medians of 10.0 and 50.1 ppm dw in the north and south arms, respectively, to a median of 75.6 ppm dw up river (Gersberg *et al.*, 1989).

Table 13.2. Comparison of median zinc concentrations (ppm dw) from the most recent non-NOAA surveys in 13 regions or sites (from Table 13.1).

Region or site	Year	Median	Ratio-to-Reference
Reference		44	
Newport shipyards	1986	295	6.7
Palos Verdes	1988	346	8.1
San Diego Harbor	1983	273	6.2
Marina del Rey	1987	215	4.9
Los Angeles-Long Beach harbors	1978	184	4.2
Upper Newport Bay	1980	113	2.6
Newport to Dana Point	1985	72	1.6
Orange County shelf	1985	54	1.2
Point Loma	1985	46	1.1
Port Hueneme to Point Dume	1985	41	0.93
Santa Barbara shelf	1985	38	0.86
Santa Monica Bay	1985	35	0.80
Bolsa Bay	1979-80	31	0.70

Using data from three synoptic coastal surveys, it is apparent that the pattern of zinc contamination along the coastal shelf did not change substantially between 1977 (Figure 13.2) and 1985 (Figure 13.3). The 1984-86 NOAA NS&T data are in substantial agreement with local and regional data (Figure 13.4). In 69 samples from 15 sites sampled in the NOAA NS&T Mussel Watch surveys, zinc concentrations ranged from 27 to 260 ppm dw (mean 92.3). This compares to 215 samples from the entire Pacific Coast with a range of 18 to 260 (mean 97.4 ppm dw; NOAA, unpublished data). The pattern, over the past decade, then, has been dominated by rather even concentrations on the order of 40 to 50 ppm dw along the entire coastal shelf with moderate local increases near Santa Barbara, in Santa Monica Bay, at one site each off Orange County and Point Loma, at several sites in San Diego Harbor, and with a substantial elevation off Palos Verdes and even greater elevations in confined channels of Newport Bay. However, at Palos Verdes, there has been very clear decreases of zinc contamination since 1974 such that by 1985, average 60-m concentrations (485 ppm dw) were within a factor of 10 background of reference concentrations (Figure 13.5). At Newport Bay shipyards mean concentrations in 1986 were within a factor of 6 of background levels (Liu and Schneider, 1988).

Based on a suite of toxicity tests, Anderson et al. (1988) computed a zinc toxicity response range of 211 to 675 ppm dw for Southern California Bight sediments. The lowest of these is about 5 times the apparent background of 44 ppm dw zinc. Median zinc concentrations in several survey areas, cited in Table 13.1, exceeded this response range and could be expected to have, or have had, levels of zinc toxic to marine life. These areas included the Palos Verdes shelf prior to 1988, Marina del Rey (1977, 1984, and 1987), sites near Newport Bay shipyards (1972, 1981, and 1986), and San Diego Harbor. At least one site each in Santa Monica Bay and Los Angeles-Long Beach harbors may also have had sediments with zinc at concentrations potentially toxic to marine organisms. The majority of the coastline surveyed did not produce sediments with zinc concentrations at or near potentially toxic levels.

From a national review of sediment effects data, Long and Morgan (1990) calculated a probable effects range (ER-L to ER-M) for zinc of 120 to 270 ppm. The lowest of these concentrations was exceeded in sediments from sites at all outfall areas, in all bays and harbors except Bolsa Bay, but was not exceeded at sites from rural coastal shelf areas. The ER-M value was exceeded only at Palos Verdes and Newport Bay.
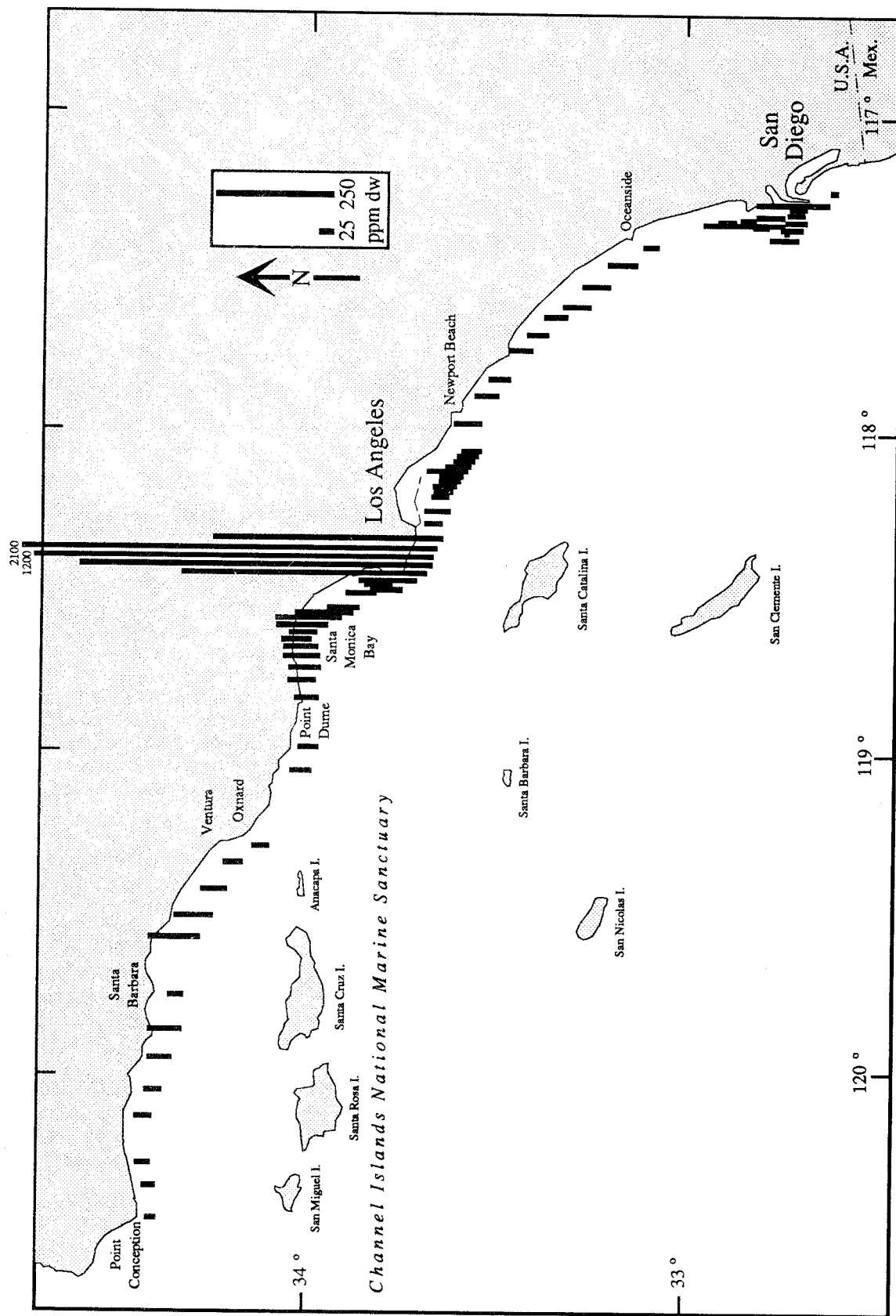
Figure 13.2. Zinc concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line, based on data from the 60-Meter Control Survey performed from April through August 1977 (Word and Mearns, 1979).
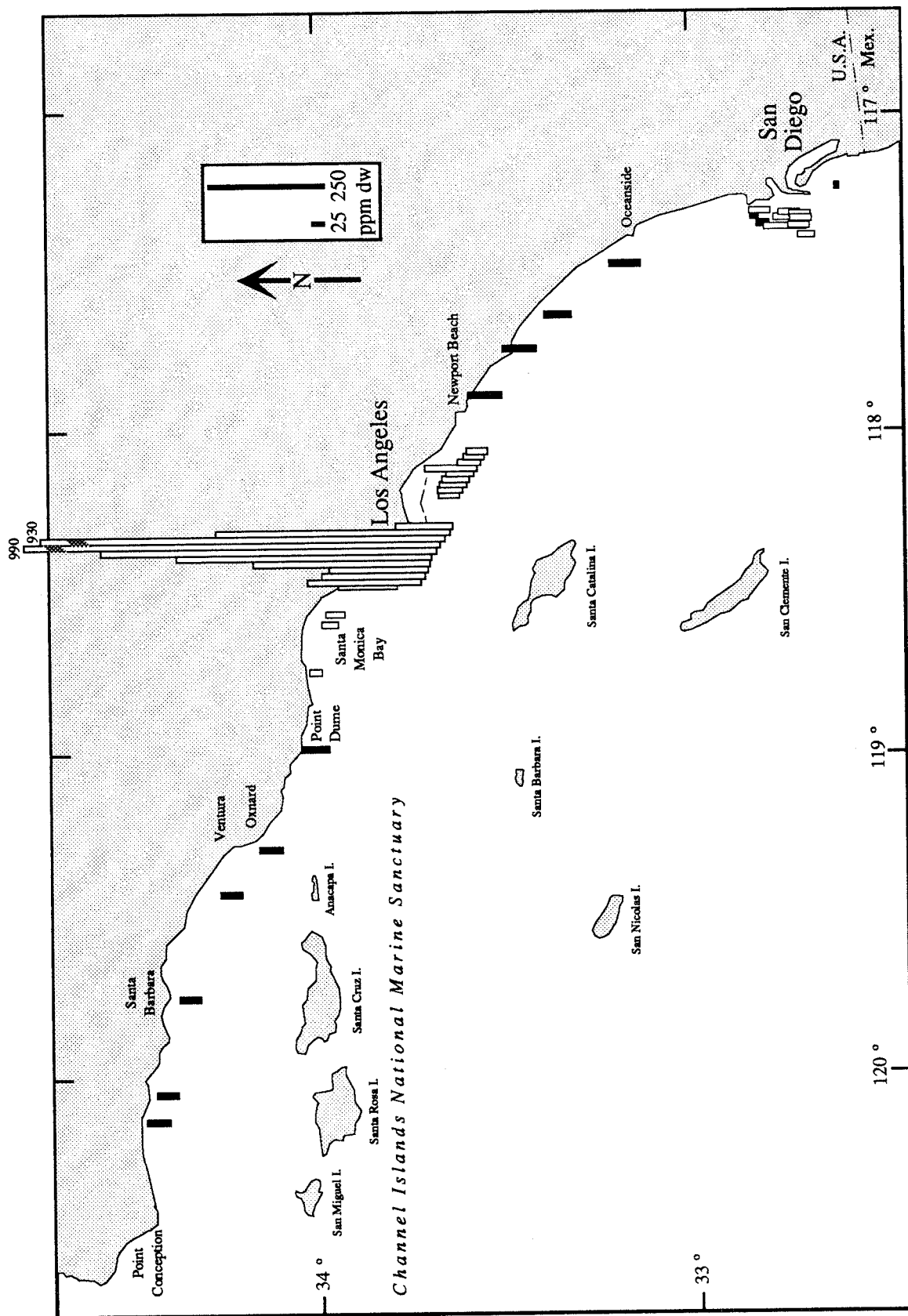
Figure 13.3. Zinc concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line for 1985; the black bars are based on data derived from Thompson et al, 1987, while the white bars are based on data obtained from the various sanitation districts (City of Los Angeles, Los Angeles, Orange, and San Diego counties).
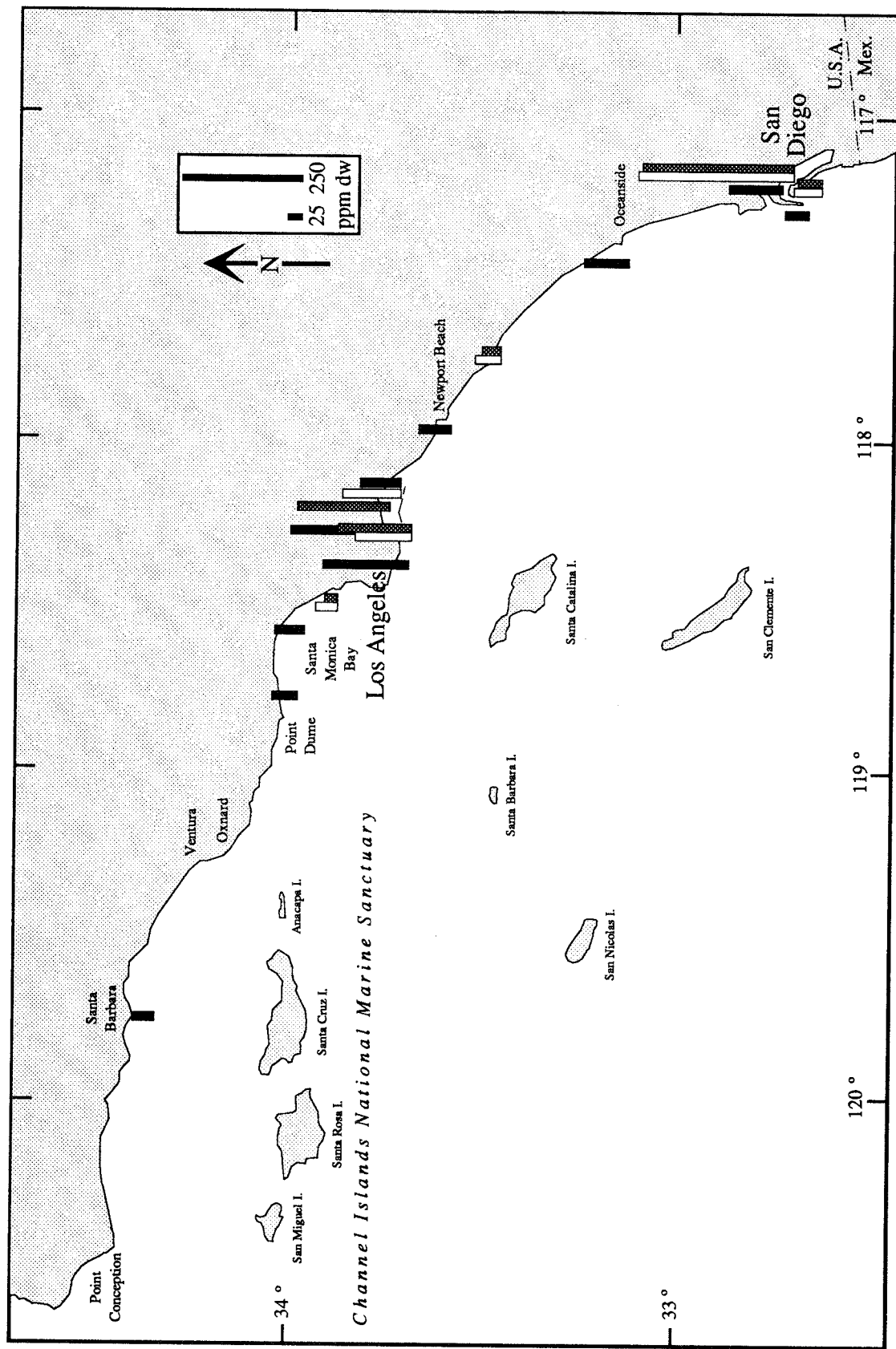
Figure 13.4. Zinc concentrations in the surficial sediments of the Southern California Bight Based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 (☐) and 1985 (☐) and Mussel Watch Project for 1986 (▮) (NOAA, 1988 and NOAA, unpublished data).
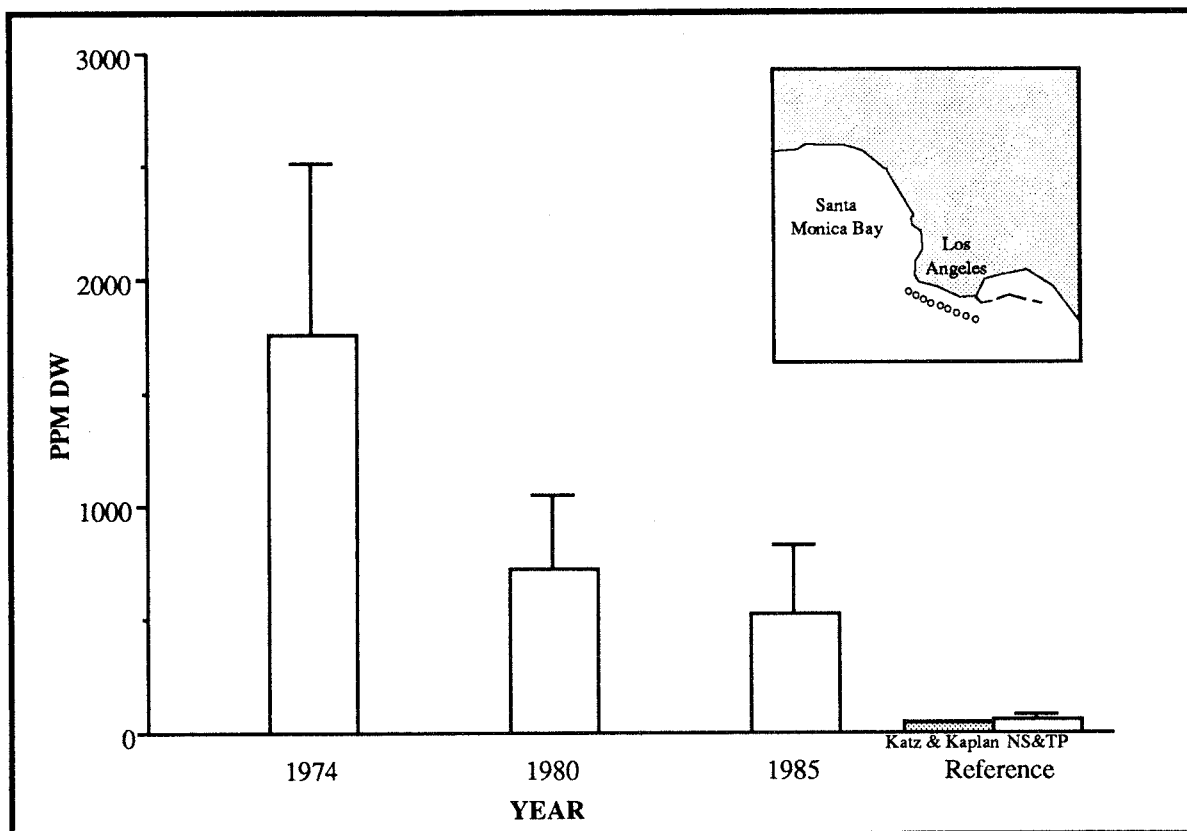
Figure 13.5. Mean zinc concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC. The reference values are based on the value reported by Katz and Kaplan (1981) and the mean of four relatively isolated NOAA NS&T Program sites in the southern California Bight sampled between 1984 and 1986 (NOAA, 1988 and NOAA unpublished data). Inset shows approximate locations of sites sampled by CSDLAC.

Long-term trends of zinc contamination in sediments of the Southern California Bight can be inferred from several time-series and dated-core studies. As noted above, zinc concentrations in surface sediments in deep water (60 m) near the Whites Point outfall have declined 10- to 20-fold between the early 1970s and 1988 (Table 13.1). This trend agrees with dramatic decreases in sewage emissions (Figure 13.1) and is also seen in data from sediment cores (Stull *et al.*, 1988). Based on data from slope and basin cores taken by Bruland *et al* (1974), Bertine and Goldberg (1977), Schmidt and Reimers (1987), and Finney and Huh (1989), zinc concentrations and fluxes in the Santa Monica and San Pedro basins were increasing from the decade 1920-30 to 1960-70 and then decreasing rapidly through the 1970s and 1980s. The last part of this trend is in good agreement with decreasing sewage emissions and sediment concentrations nearshore (at Whites Point). However, a different trend may have occurred in bays and lagoons. Christensen *et al.* (1978) reported that zinc concentrations in sediments of Upper Newport Bay began increasing noticeably in 1955 and continued to the mid-1970s, a pattern similar to that for lead. These patterns suggest that bays and lagoons were becoming increasingly contaminated, possibly from run-off (automobile tire wear); while offshore areas were recovering from zinc contamination. Nonetheless, one of the most dramatic episodes of sediment zinc contamination and decline was in the Rhine Channel of Lower Newport Bay where disposal of vessel paint scrapings resulted in sediment concentrations as high as 13,700 ppm dw in 1972. As a result of paint yard controls enforced by the Santa Ana Regional Water Quality Control Board, mean sediment zinc concentrations near these shipyards decreased from 3376 ppm dw in 1972 to 264 ppm dw in 1986.

In summary, data collected over the past decade indicate that while high zinc concentrations (10 times background levels) prevailed off Palos Verdes in past years, this site was atypical of other coastal shelf wastewater discharge areas where increases have been less than twice background levels. Three of four harbor and bay areas (San Diego Harbor, Los Angeles-Long Beach harbors, and Marina del Rey) have experienced mean concentrations 5 to 10 times coastal reference values. There is evidence of long-term decreasing concentrations at Palos Verdes, little change at Marina del Rey, and possible increases in Upper Newport Bay. There is also evidence that zinc concentrations increase landward in two lagoons (Newport Bay and Tijuana estuary). Evidence is lacking to document trends in other bays and harbors, or to confirm what trends really have been like in the 1980s.

ZINC IN MUSSELS

Although sediments in several areas of the Bight have experienced dramatic (1,000-fold) gradients of zinc contamination, there have been no similar gradients in mussels.

In these surveys, there was a tendency for zinc to be higher in *M. edulis* than in *M. californianus*. Graham (1972) measured body burdens of zinc in *M. edulis* and *M. californianus* specimens collected at the same location and found that higher concentrations occurred in *M. edulis*. Analyses conducted by the CMW Program on *M. edulis* and *M. californianus* collected at the same site also showed a higher zinc concentration in *M. edulis*, but the difference was not significant (Hayes *et al.*, 1985).

Results for zinc concentrations in discrete tissues of *M. edulis* obtained by Young and McDermott (1976) indicated that no significant differences existed among digestive gland, gonad, muscle, or other remaining tissues. This contrasted with observed results for other metals such as copper, chromium, nickel, or lead which appeared to accumulate preferentially in digestive gland tissue. Lobel (1986) examined zinc accumulation in *M. edulis*, attempting to minimize or eliminate all known physiological or environmental factors that might contribute to variability, and still found a very high (coefficient of variation approximately 40 percent) inherent variability in whole soft tissue concentrations. Furthermore, while most individual organs had relatively low zinc concentrations with low variability, the kidney showed much higher concentrations (mean, 828 ppm) with much greater variability (94 to 3410 ppm, coefficient of variation, 78%). Lobel concluded that kidney concentrations of zinc were responsible not only for most of the whole tissue concentrations, but also for variability within the population as a whole.

In a 1971 *M. californianus* survey at 19 stations, concentrations in digestive glands varied only threefold, from 46 ppm in samples from the Newport Bay jetty to 110 ppm dw in samples from Santa Barbara Island. There was no evidence of higher concentrations near urban areas such as Los Angeles or San Diego (Figure 13.6; Alexander and Young, 1976).

Subsequent surveys using whole soft tissue excluding gonads (California Mussel Watch, 1977-86) and whole soft tissue (NOAA NS&T Program, 1986-88) have also not revealed any strong regional gradients of zinc contamination. In mussels collected from southern California between 1977 and 1985 by the CMW, concentrations in 121 *M. californianus* samples (mainly from open coastal sites) ranged fourfold from 90 to 337 ppm dw (mean, 177 ppm dw; Table 13.3) and in 41 resident *M. edulis* (mainly from bays and harbors) concentrations ranged about sevenfold, from 80 to 557 ppm dw. The highest concentration (557 ppm dw) occurred in a sample of mussels from Oceanside Harbor in 1985 (Table 13.4). In *M. edulis* and *M. californianus* there appeared to be slightly higher concentrations in mussels from the Santa Monica Bay area (including Point Dume) than elsewhere. For example, *M. californianus* levels were 140 to 270 ppm dw in 10 Santa Monica Bay samples compared to 103 to 200 ppm dw in samples from other areas sampled in 1980 (Table 13.3). In the 1986 NOAA NS&T Mussel Watch Project, zinc concentrations ranged from 133 ppm dw in *M. californianus* from near Bird Rock, Santa Catalina Island, to 310 ppm dw in *M. edulis* from the Marina del Rey jetty (Figure 13.7).
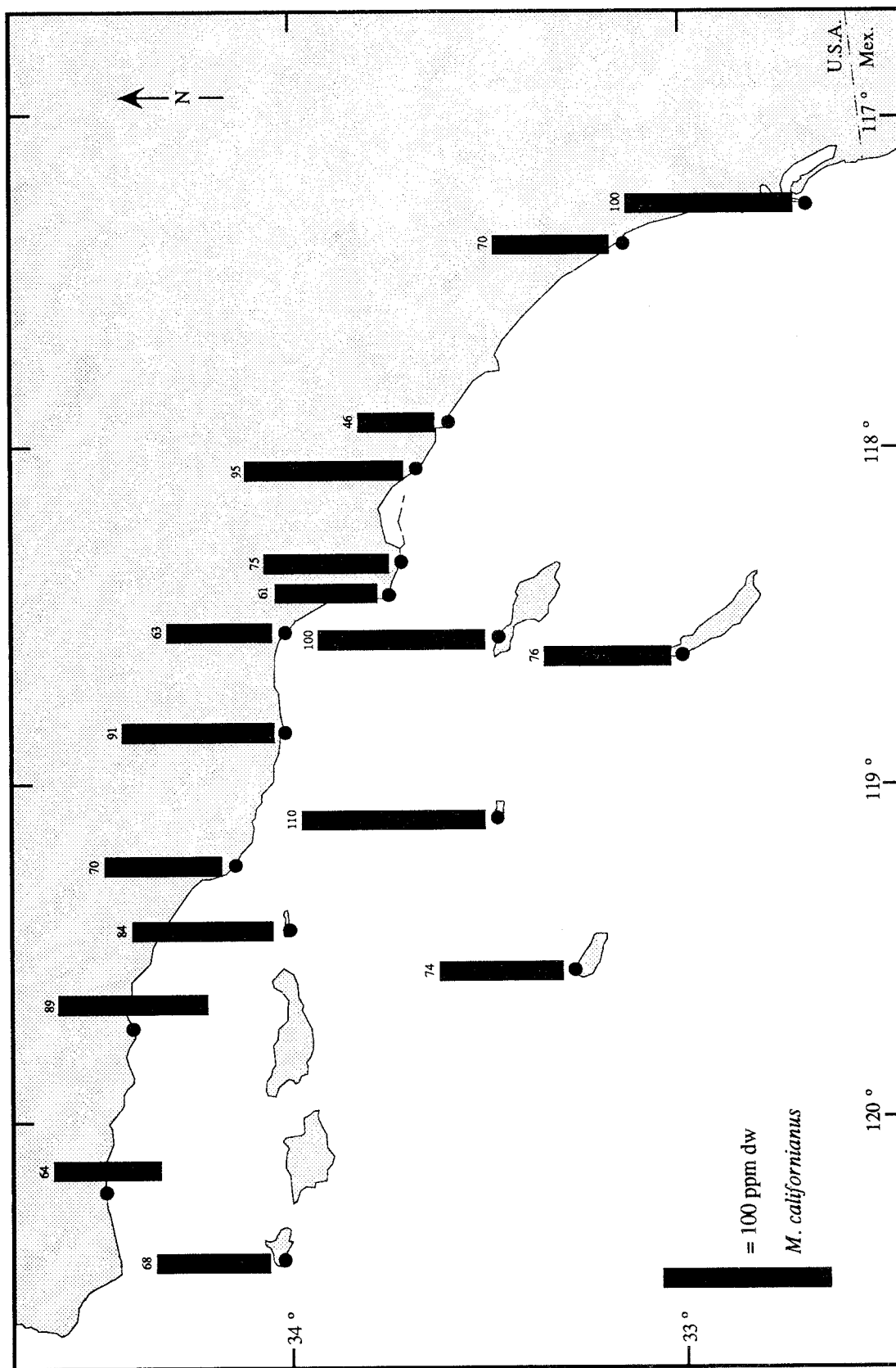
Figure 13.6. Zinc in digestive gland of mussels sampled in 1971. Values shown are means of six samples, each sample = one individual. Source: Young, 1974.

Table 13.3. Summary of zinc concentrations (ppm dw) in whole *M. californianus* from various sampling areas in the Southern California Bight, 1980 and 1986 (Phillips, 1988 and NOAA, 1989).

Region or site	Year	N	Mean	Median	Minimum	Maximum	Stamdard Deviation	Source*
Southern California	1977-85	121	177	170	90	337	58	CMW
Santa Monica Bay	1980	10	196	200	140	270	35	CMW
Santa Catalina Island	1980	5	135	125	103	182	32	CMW
Newport to Imperial Beach	1980	13	145	140	110	200	27	CMW
Point Dume	1986	3r	193	190	180	210	—	NS&T
Santa Barbara/Islands	1986	3	148	153	133	157	—	NS&T
All coastal sites	1986	8	163	159	133	197	19	NS&T

*CMW = Phillips, 1980; NS&T = NOAA, 1989

Table 13.4. Summary of zinc concentrations (ppm dw) in whole *M. edulis* from various sampling areas in the Southern California Bight, 1980 and 1986 (Phillips, 1988 and NOAA, 1989).

Region or site	Year	N	Mean	Median	Minimum	Maximum	Standard Deviation	Source*
Southern California	1980-85	41	258	220	80	557	41	CMW
Channel Islands Harbor Oxnard	1980	1	180	—	—	—	—	CMW
Marina del Rey	1980, 1982	2	409	409	340	477	—	CMW
Marina del Rey jetty	1986	3r	310	320	280	330	—	NS&T
Los Angeles-Long Beach harbors	1982-85	17	292	300	146	450	95	CMW
San Pedro Bay Breakwater	1986	3r	180	160	150	230	—	NS&T
Colorado Lagoon Long Beach	1982, 1985	3	133	111	110	179	—	CMW
Anaheim Bay Long Beach	1980, 1982	2	249	249	147	350	—	CMW
Newport Bay	1980, 1982	4	333	357	137	480	145	CMW
Newport pier	1980	1	129	—	—	—	—	CMW
Oceanside Harbor	1985	1	557	—	—	—	—	CMW
Mission Bay	1980, 1982	5	154	160	99	180	32	CMW
Point Loma	1983	1	162	—	—	—	—	CMW
San Diego Harbor	1980, 1982	4	198	230	80	250	79	CMW
San Diego Harbor Island	1960	3r	273	270	260	290	—	CMW

r = replicate samples from the same site
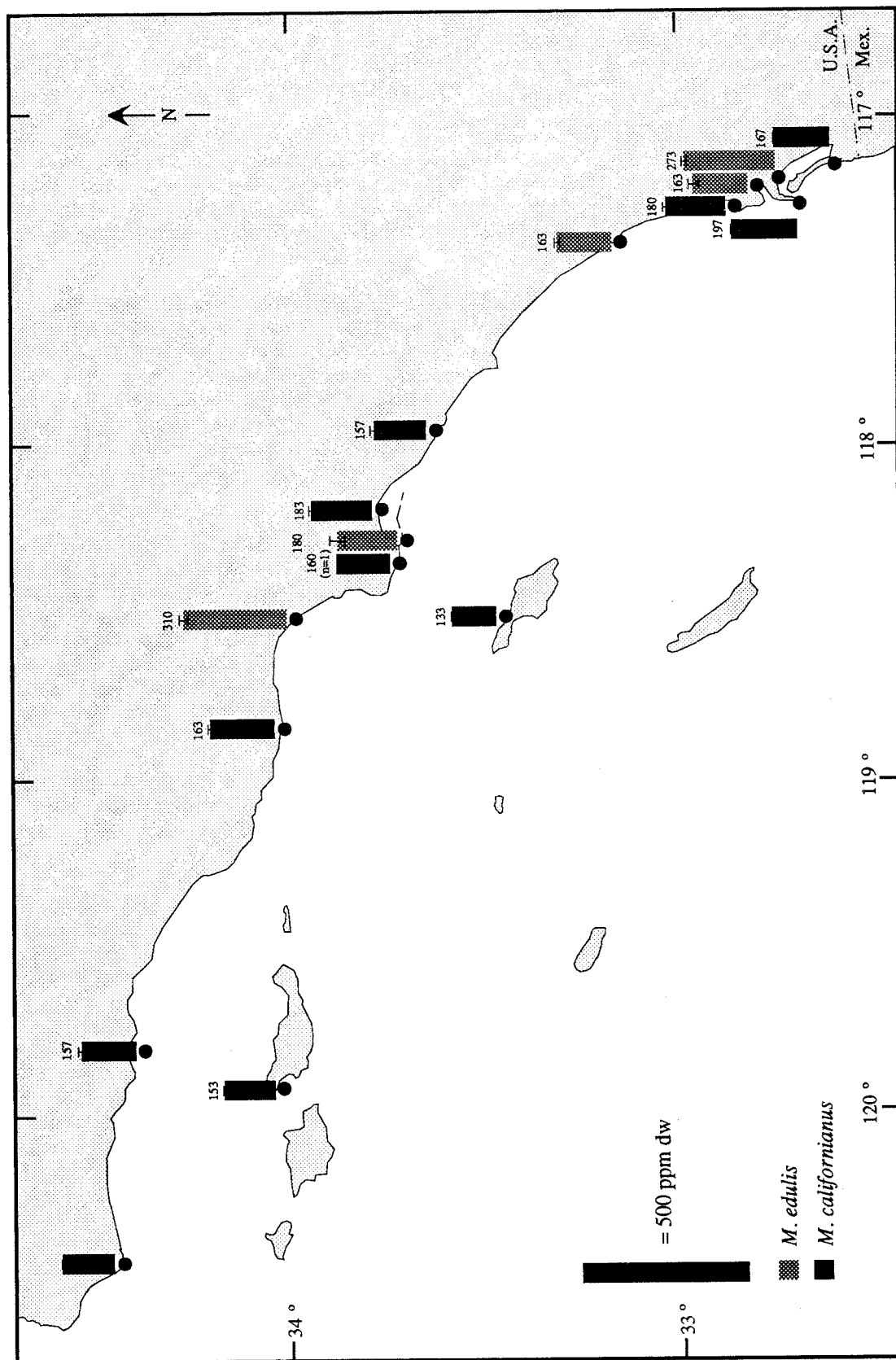*CMW = Phillips, 1980; NS&T = NOAA, 1989

Figure 13.7. Zinc in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

13-13

Many of the higher tissue concentrations occurred in harbor or marina locations, where reduced flushing and a greater number of vessels than in other areas could be expected. Elevated zinc concentrations may be a result of species differences between *M. edulis* and *M. californianus* in accumulation of the element, or a result of relatively higher environmental concentrations of zinc in harbor/marina areas. However, Young, Jan, and Hershelman (1980) attribute the high zinc levels they observed in mussels from California yacht harbors to corrosion protection devices (sacrificial zinc anodes) and paints and primers from vessels.

Despite the absence of regional gradients, there may have been local gradients of zinc contamination in mussels within harbors. For example, in Los Angeles-Long Beach harbors and in the San Diego Harbor area sampled in 1974 by Young *et al.* (1975), zinc concentrations were slightly higher at inner harbor stations (Figure 13.8). An intensive 1982 CMW survey in Los Angeles-Long Beach harbors suggested concentrations were higher by perhaps 50 percent at inner harbor sites than at middle harbor sites (Figure 13.9).

Several bays and harbors received intensive surveys during the early 1980s. In Santa Monica Bay, at 10 sites surveyed in 1980, the mean zinc concentration in *M. californianus* was 196 ppm dw (range 140 to 270). These levels are comparable to those found throughout southern California by CMW (mean 177, range 90 to 337 ppm dw), slightly higher than concentrations for Santa Catalina Island (mean 135, range 103 to 182 ppm dw) and on the coastal shelf between Newport Beach and Imperial Beach (mean 145, range 110 to 200 ppm dw; Table 13.3). Results from the 1986 NOAA NS&T *M. californianus* samples show similar patterns with slightly higher concentrations at Point Dume (193 ppm dw) than at other sites (Table 13.3). Thus, zinc concentrations in *M. californianus* have been slightly higher (by 25 to 30 percent) in Santa Monica Bay than at other sites in the Bight.

Marina del Rey (mean 409 ppm dw) and Oceanside Harbor (557 ppm dw) were the most contaminated embayments with respect to zinc in *M. edulis* (Table 13.4). Concentrations were also moderately high in *M. edulis* from Newport Bay (333 ppm dw), Los Angeles-Long Beach harbors (292 ppm dw), and San Diego's Harbor Island (273 ppm dw; Table 13.4). In Los Angeles-Long Beach harbors, concentrations were higher at sites in inner harbor areas (240 to 450 ppm dw) than at middle harbor sites (150 to 300 ppm dw; Figure 13.9). The average concentration for all 1980-85 resident *M. edulis* samples from southern California was 258 (range 80 to 557) ppm dw. The lowest concentrations, on the order of 125 to 175 ppm dw, occurred in the Colorado Lagoon (Long Beach), at Newport Pier, in Mission Bay, and at Point Loma (Table 13.4).

The overall mean levels of zinc in *M. edulis* and *M. californianus* (152.46 and 152.34 ppm dw, respectively) sampled at all sites by NOAA's NS&T Program between 1986 and 1989 are nearly identical. These mean values are similar to those found at southern California sites. Overall national median values were higher in *M. californianus* (153.33 ppm dw) than in *M. edulis* (113.33 ppm dw).

There have been no dramatic long-term trends of zinc in mussels. Although emissions from municipal wastewater discharges have declined steadily since 1971 (Figure 13.1), zinc in tissue of *M. californianus* from long-term monitoring sites of the CMW Program do not reflect such trends (Figure 13.10). This stands in contrast to time-series analyses of other metals in mussel tissue, such as lead, in which body burdens show decreases corresponding to decreases in dominant source inputs.

However, results from the CMW Program shown in Figure 13.10 suggest that concentrations of zinc in *M. californianus* collected at Royal Palms, inshore from the JWPCP outfall on the Palos Verdes Peninsula, consistently exceeded those in mussels from Oceanside. Although this would be expected, given the magnitude of zinc discharges from that plant and the recognized propensity for mussels to accumulate zinc in tissue, other data sets analyzed for this discussion (1974 SCCWRP; 1976-78 EPA Mussel Watch; other 1977-1985 CMW data; 1986 NS&T Mussel Watch; and the 1971 SCCWRP data discussed previously, failed to demonstrate marked regional trends in zinc tissue concentrations associated with this discharge. An apparent long-term increase at Oceanside (Figure 13.10) may merit attention.

In the first 3 years of sampling by the NS&T Mussel Watch, only two sites showed significant changes in zinc concentrations. Mussels from Imperial Beach, south of San Diego and Anaheim Bay near Long Beach showed declines in levels of zinc between 1986 and 1988 (NOAA, 1989).

Figure 13.8. Zinc in digestive gland of mussels sampled in 1974. Source: Young et al., 1979; Young, unpublished.
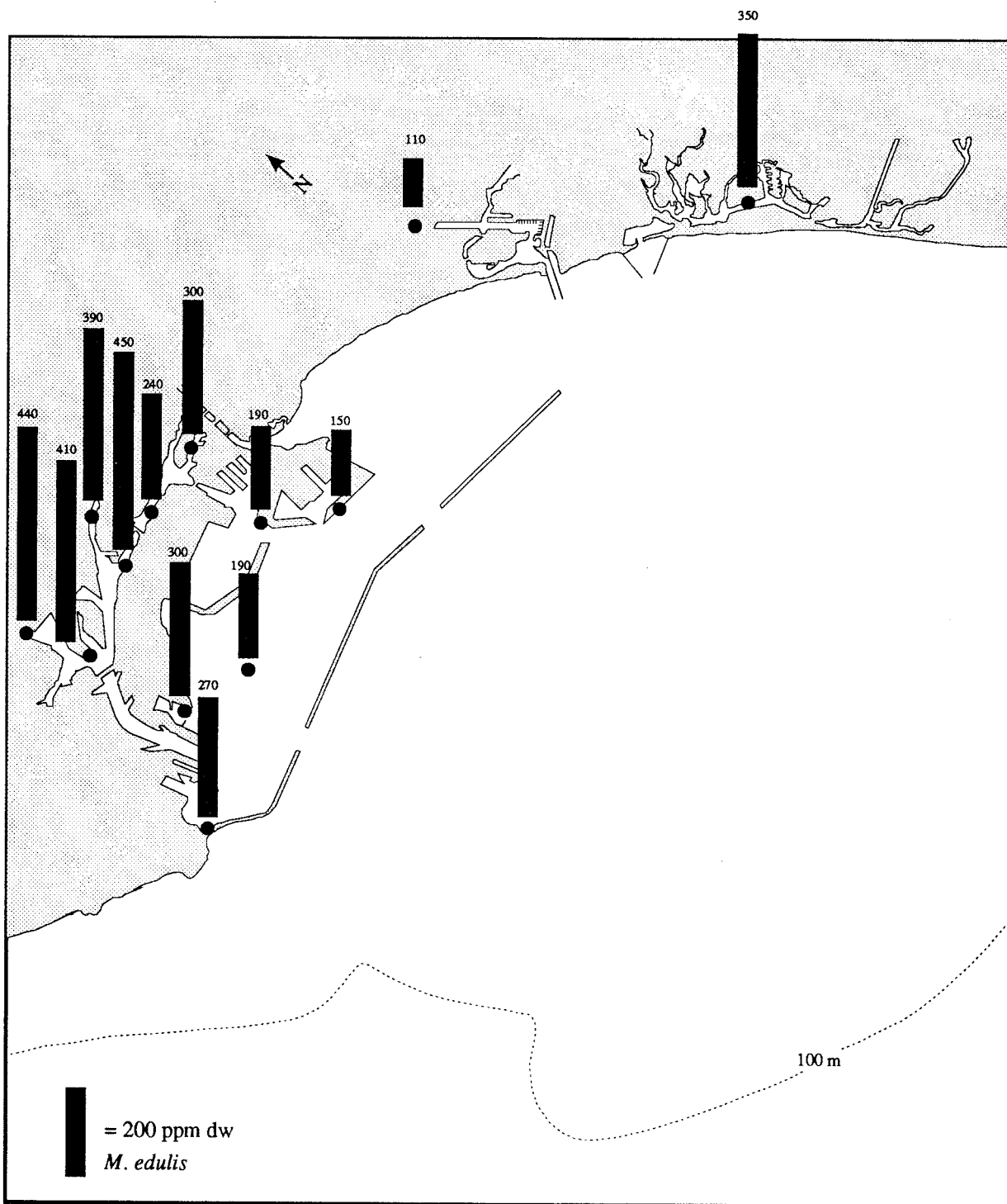
Figure 13.9. Zinc in whole soft body tissue, excluding gonads, of mussels sampled in San Pedro Bay in 1982. Source: Phillips, 1988.
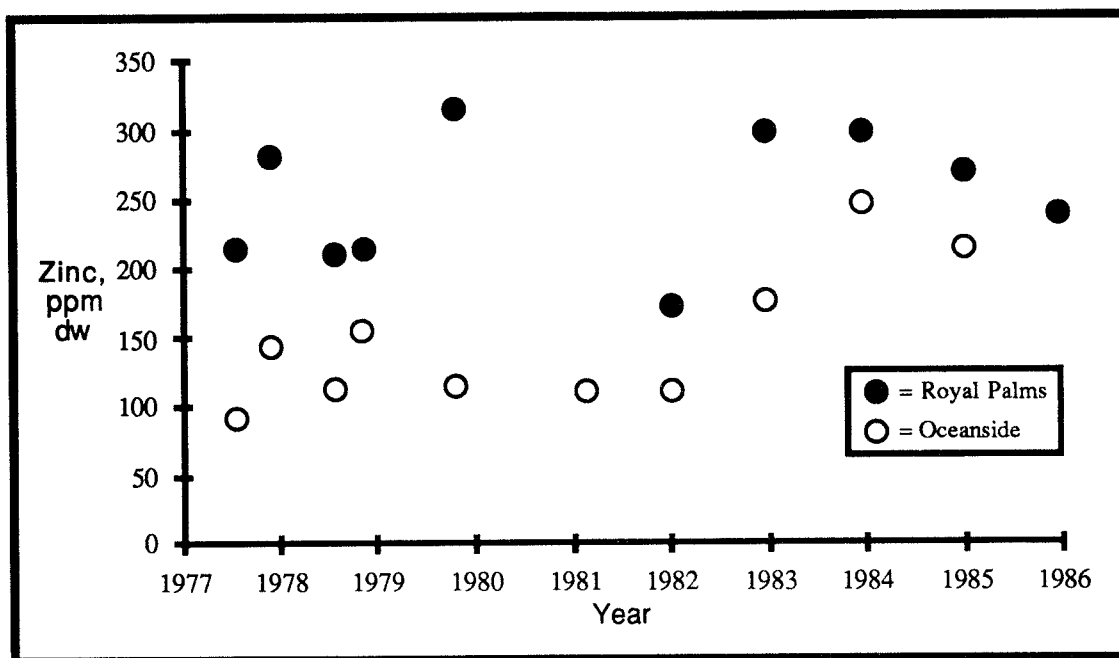
Figure 13.10. Time series of zinc concentrations measured in *M. californianus* mussels collected at Royal Palms and at Oceanside, 1977-85. Source: Phillips, 1988.

In summary, zinc in mussels has not experienced large gradients of contamination in the Southern California Bight. There is evidence of 2- to 3-fold increases within Los Angeles-Long Beach and several other harbors and 25 to 30 percent increases near the Palos Verdes outfalls. Interannual variations of zinc at several sites do not follow the downward trend of zinc input from sewage.

ZINC IN FISH AND OTHER SPECIES

In a survey of 30 southern California marine organisms conducted by one laboratory (SCCWRP), concentrations of zinc in non-hepatic tissues (mainly muscle) ranged from 0.6 ppm ww in muscle of a California scorpionfish to 210.0 ppm in muscle of a yellow crab. Both were collected from Dana Point in 1976 (Table 13.5). In general, concentrations in invertebrates (4.3 to 210 ppm ww) were higher than concentrations in fish and sharks (0.6 to 19.5 ppm ww; Table 13.5) suggesting zinc does not undergo biomagnification in southern California marine food webs. This was confirmed when data from these organisms were tested against a trophic increase model. In some local food webs, zinc may experience decrease with trophic level (Young, 1988).

From a 1975-77 investigation, Young *et al.* (1978) found that in all the 12 popular seafood invertebrates and fishes sampled zinc concentrations in edible tissue of specimens from the Palos Verdes wastewater discharge were not significantly higher than in comparable specimens from remote distant or island control areas. In some species, specimens from Palos Verdes were slightly to severely depleted in zinc relative to reference site specimens (red sea urchin, yellow crab, spiny lobster).

There were a few cases where zinc concentrations seemed to be elevated compared to reference sites (Table 13.5). Muscle of white croaker at three sites along the Los Angeles-Orange County coast (means 3.22 to 3.72 ppm ww) contained more zinc in 1975-76 relative to fish from Dana Point (1.47 ppm ww). Muscle of California halibut from two sites between Point Dume and Los Angeles Harbor (means 2.39 to 3.37 ppm ww) seemed to contain more zinc than a San Diego collection in 1976 (mean 1.90 ppm ww). Muscle of bocaccio at Palos Verdes (mean, 4.71 ppm ww of zinc) was elevated in zinc relative to fish from San Clemente Island in 1975-79 (1.89 ppm ww). Table 13.5 also shows the possible depletion of zinc in muscle of ridgeback prawn and yellow crab at Palos Verdes (means 9.65 and 26.17 ppm ww, respectively) versus specimens from remote sites in 1975-76 (up to 11 and 113.5 ppm ww, respectively). Additional sampling is needed to confirm these deviations that are generally less than a factor of 2 between sites.

Table 13.5. Zinc concentrations (ppm ww) in edible tissues of marine organisms from the Southern California Bight

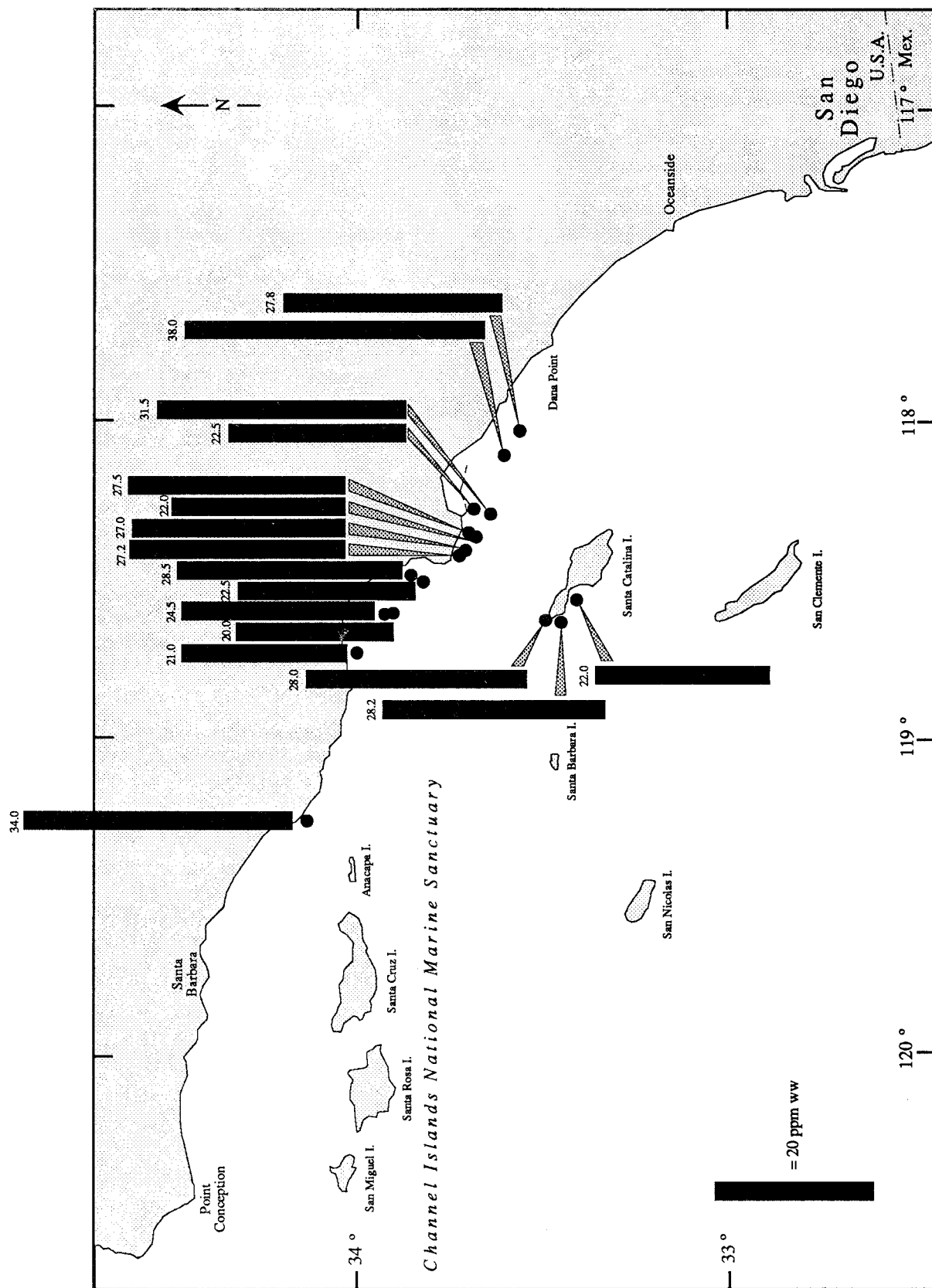| Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	Source
Kelp	Los Angeles Harbor	1980	5	5.99	6.01	5.21	6.69	0.58	Mearns and Young, 1980
Mysids (whole)	Palos Verdes	1980	8	10.41	10.03	5.03	17.30	4.35	Schafer et al., 1982
Zooplankton (whole)	Coastal	1980-81	5	10.54	9.60	7.09	14.70	2.88	Schafer et al., 1982
Black Abalone	San Clemente	1975	7	7.81	7.84	5.29	9.36	1.42	Young et al., 1978
	Dana Point	1975	4	8.89	9.72	5.61	10.50	2.23	Young et al., 1978
	Whites Point	1976	5	5.72	6.12	4.28	6.60	1.00	Young et al., 1978
	Santa Catalina Island	1975-77	3	9.11	9.00	7.62	10.70	1.54	Young et al., 1978
Gaper Clams	Los Angeles Harbor	1980	5	8.91	8.54	7.62	10.50	1.27	Mearns and Young, 1980
Market Squid	Coastal	1980-81	3	9.72	9.59	8.78	10.80	1.02	Schafer et al., 1982
Purple-hinge Scallop	Santa Barbara	1973	2	21.70	-	21.10	22.30	0.85	Young et al., 1978
	Santa Catalina Island	1973-74	4	21.93	21.30	20.10	25.00	2.13	Young et al., 1978
	Laguna -Scottsman Cove	1975	9	9.73	9.84	6.48	12.70	2.03	Young et al., 1978
	Palos Verdes	1976	8	19.86	19.85	17.60	22.00	1.52	Young et al., 1978
	Dana Point	1976	1	11.80	-	-	-	-	Young et al., 1978
California Spiny Lobster	Cortez Bank	1975	1	15.00	-	-	-	-	Young et al., 1978
	Point Dume	1976	2	9.16	9.16	8.47	9.85	0.98	Young et al., 1978
	Santa Catalina Island	1976	9	15.54	16.00	10.20	20.50	3.76	Young et al., 1978
	Laguna -Abalone Point	1976	1	11.40	-	-	-	-	Young et al., 1978
	San Diego	1977	3	11.90	12.00	11.00	12.70	0.85	Young et al., 1978
	Bunker Point	1975-77	5	8.81	8.01	5.76	11.46	2.35	Young et al., 1978
Ridgeback Prawn	Palos Verdes	1976	3	9.65	9.85	9.17	9.94	0.42	Young et al., 1978
	Santa Catalina	1976	10	8.79	8.59	5.98	13.90	2.24	Young et al., 1978
	Orange County	1975-76	3	10.58	10.00	7.31	17.70	2.89	Young et al., 1978
	Palos Verdes	1980	5	12.00	11.90	10.60	13.70	1.18	Mearns and Young, 1980
Yellow Crab	Orange County	1975	3	32.90	33.70	19.00	46.00	13.52	Young et al., 1978
	Palos Verdes	1975-76	9	26.17	25.20	20.80	39.80	5.70	Young et al., 1978
	Dana Point	1976	3	113.53	96.90	33.70	210.00	89.32	Young et al., 1978
Boccacio	Palos Verdes	1973	1	3.90	-	-	-	-	Young et al., 1978
	Palos Verdes	1975-79	7	4.71	4.80	3.80	5.40	0.62	Young et al., 1978
	San Clemente Island	1977	3	1.89	1.90	1.65	2.12	0.24	Young et al., 1978
California Halibut	San Diego	1976	2	1.90	1.90	1.89	1.90	0.01	Young et al., 1978
	Palos Verdes	1976	4	3.27	2.80	2.31	5.08	1.24	Young et al., 1978
	Point Dume	1976	2	2.39	2.39	2.21	2.56	0.25	Young et al., 1978
	Los Angeles Harbor	1980	4	2.28	2.16	1.87	2.92	0.45	Mearns and Young, 1980
California Scorpionfish	Santa Catalina Island	1974	3	3.70	3.40	3.30	4.41	0.61	Young et al., 1978
	Palos Verdes	1974-75	9	4.10	3.90	2.40	6.50	1.17	Young et al., 1978
	Orange County	1974-76	10	4.21	3.95	3.31	6.19	0.88	Young et al., 1978
	Dana Point	1976	5	1.78	1.98	0.60	2.46	0.79	Young et al., 1978
	Palos Verdes	1980	4	2.54	2.33	1.83	3.67	0.79	Schafer et al., 1982
Dover Sole	Palos Verdes	1980	5	2.86	2.70	2.47	3.74	0.52	Schafer et al., 1982
Northern Anchovy	Los Angeles Harbor	1980	5	5.23	4.62	3.86	6.73	1.27	Mearns and Young, 1980
	Coastal	1980-81	5	7.60	8.90	4.30	9.40	2.19	Schafer et al., 1982
Pacific Bonito	Coastal	1980-81	5	3.90	3.54	2.64	5.72	1.15	Schafer et al., 1982
Pacific Hake	Coastal	1980-81	5	2.59	2.57	2.20	2.90	0.27	Schafer et al., 1982
Pacific Mackerel	Coastal	1980-81	6	4.40	4.45	3.90	4.90	0.44	Schafer et al., 1982
Pacific Sanddab	Santa Catalina Island	1973	3	4.26	3.98	2.70	6.10	1.72	Young et al., 1978
	Palos Verdes	1975-76	9	3.66	3.40	1.90	6.70	1.49	Young et al., 1978
Pacific Sardine	Coastal	1980-81	5	3.94	3.55	3.49	4.69	0.58	Schafer et al., 1982
Spotted Sand Bass	Newport Bay	1978	3	4.01	4.26	3.31	4.47	0.62	Mearns and Young, 1980
Striped Bass	Newport Bay	1978	3	4.11	4.10	3.37	4.86	0.75	Mearns and Young, 1980
Striped Mullet(adult)	Newport Bay	1978	3	3.24	3.32	3.01	3.38	0.20	Mearns and Young, 1980
Striped Mullet(juv.)	Newport Bay	1978	3	2.96	2.91	2.71	3.26	0.28	Mearns and Young, 1980
Swordfish	Coastal	1980-81	5	6.44	6.20	5.32	7.63	0.93	Schafer et al., 1982
Topsmelt	Newport Bay	1978	3	13.89	13.80	8.37	19.50	5.57	Mearns and Young, 1980
White Croaker	Palos Verdes	1975	8	3.72	3.38	2.40	5.52	1.11	Mearns and Young, 1980 Young et al., 1978
	Orange County	1975	10	3.22	2.97	2.17	6.43	1.21	Young et al., 1978
	Dana Point	1976	5	1.47	1.38	1.24	1.84	0.24	Young et al., 1978
	Los Angeles Harbor	1980	5	3.35	3.47	2.96	3.51	0.23	Mearns and Young, 1980
	Palos Verdes	1980	5	2.10	1.87	1.33	3.53	0.90	Schafer et al., 1982
Yellowfin Croaker	Newport Bay	1978	3	5.71	5.75	4.09	7.30	1.61	Mearns and Young, 1980
Mako Shark	Coastal	1980-81	5	5.34	3.90	2.70	11.00	3.37	Schafer et al., 1982
Spiny Dogfish	Palos Verdes	1980	5	3.85	3.75	3.42	4.49	0.42	Schafer et al., 1982
Thresher Shark	Coastal	1980-81	5	4.05	4.02	3.56	4.76	0.52	Schafer et al., 1982
White Shark	Coastal	1980-81	3	5.05	4.34	3.96	6.84	1.57	Schafer et al., 1982

Anderlini (1974) was unable to identify geographic gradients of zinc in four tissues of red abalone (*Haliotis refescens*) samples in 1971 from five subtidal sites in northern and southern California. However, his data suggests that levels in red abalone digestive gland might have been higher at the two southern California sites (Long Beach 752 and La Jolla 980 ppm dw) than at two of the three northern California sites (Mendocino, 555 and Shelter Cove, 536 ppm dw).

In kelp bass collected in the mid-1960s from the intake well of the Scattergood Power Plant (Santa Monica Bay), which may have been a source of zinc, and from Santa Catalina Island, the highest zinc concentrations occurred in eye tissue (600 to 700 ppm dw), skin (190 to 223 ppm dw), and gonad (119 to 245 ppm dw). Lower concentrations occurred in liver (60 to 100 ppm dw), heart (82 to 90 ppm dw), and muscle (9 to 26 ppm dw; Stapleton, 1968). In this study, zinc concentrations in muscle were much higher in fish from the power plant (15 to 26 ppm dw or about 3 to 5 ppm ww) than in those from Catalina (9 to 10 ppm dw or about 1.8 to 2.0 ppm ww). It is possible that zinc may have undergone bioaccumulation in muscle of fish in confined areas under special conditions.

Livers of Dover sole from 17 coastal and island sites contained a narrow range of zinc concentrations (21 to 38 ppm ww; Figure 13.11) considering the fact that many of these fish were taken from areas where sediments contain zinc concentrations more than 10 times above background levels (such as shown in Figure 13.2). The same lack of obvious zinc increases in fish liver was also apparent in composites from three species of fish from six NOAA NS&T Benthic Surveillance sites sampled in 1984 (Figure 13.12). The highest concentrations for hornyhead turbot were in fish from the Dana Point reference site and a site in San Diego Bay (outside the harbor). Even within San Diego Bay and Long Beach Harbor (Seal Beach) where average sediments contained approximately 2 to 5 times more zinc than comparable coastal reference sites, barred sand bass and white croaker contained similar levels of zinc as in specimens from the Dana Point site (Figure 13.12). Curiously, in the Stapleton (1968) study, zinc was lower (61 ppm dw) in kelp bass liver from a power plant intake well in Santa Monica Bay (a presumed metal source) than in fish from Santa Catalina Island (100 ppm dw).

There are no action levels or quality criteria for zinc in U.S. seafood organisms. However, Nauen (1983) reported two foreign criteria: 40 and 100 ppm ww (mean, 70 ppm). Only muscle of some yellow crab from Dana Point and Orange County in 1975 or 1976 approached or exceeded the minimum of 40 ppm ww. Most fish, regardless of site, had concentrations an order of magnitude lower than the minimum (Table 13.5).

Zinc is now routinely monitored in fish and large invertebrates from sewage outfall discharge sites off Orange County, in Santa Monica Bay, and at other sites in Ventura and Santa Barbara counties. Although much of this data is unpublished, they should not be ignored in future assessments.

Figure 13.11. Zinc concentrations in liver tissue of Dover sole collected in the Southern California Bight in 1971 and 1972. Source: de Goeij et al. (1974).
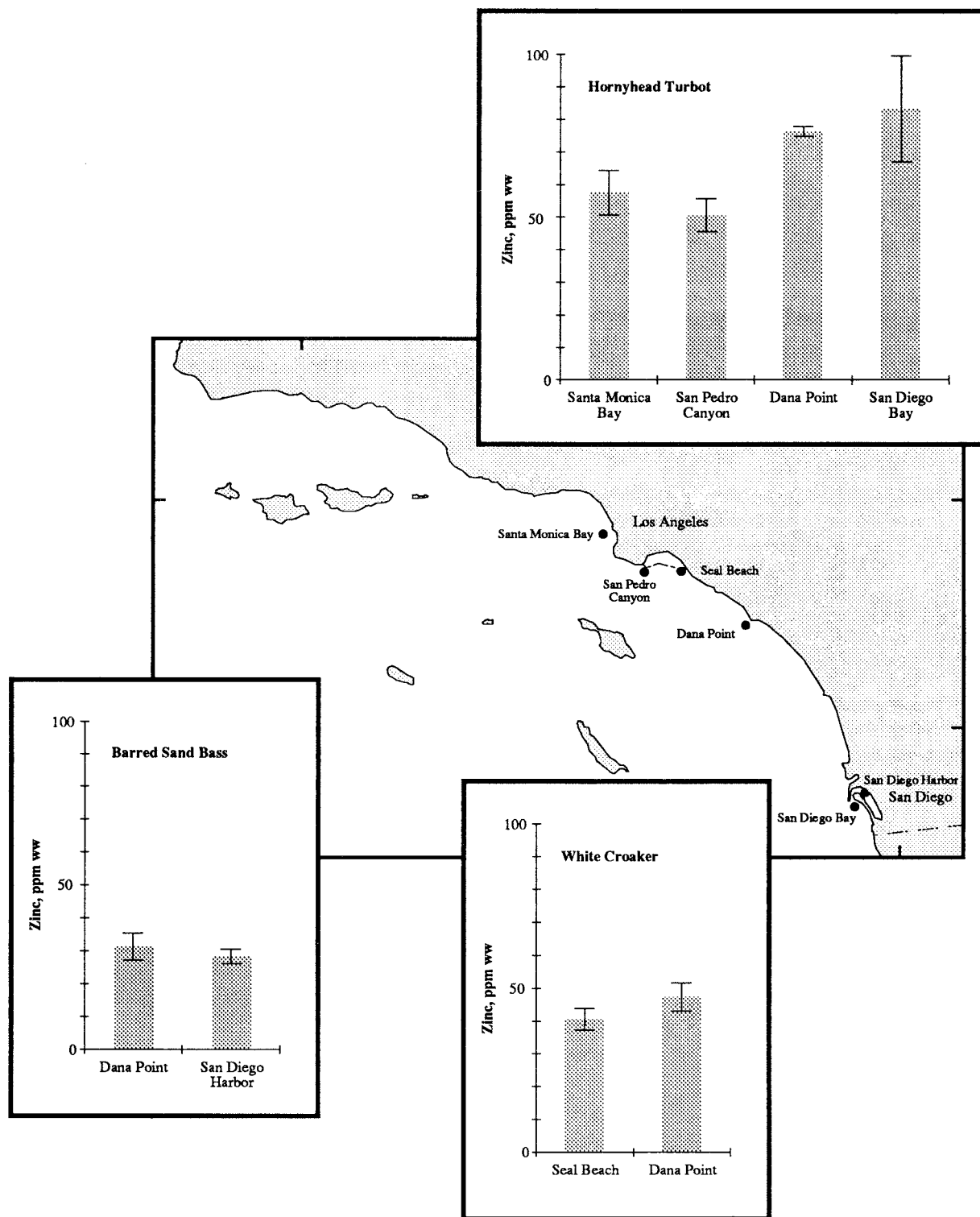
Figure 13.12. Concentrations of zinc measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.

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SUMMARY AND CONCLUSIONS

Like many other trace elements reviewed for this report, zinc presents a dilemma. Huge quantities have been discharged to the coastal zone through sewage and run-off and possibly from vessel paints and aerial fallout. In the past, minor sources included direct fallout from brush fires. Historically, zinc has accumulated in extremely high concentrations (100 to 1000 times background) in sediments at several localized nearshore areas (Palos Verdes, Rhine Channel, Newport Bay, and a site in San Diego Harbor), possibly exceeding levels toxic to benthic organisms. Zinc also increased to moderate, but non-toxic, concentrations (2 to 5 times background) in sediments of offshore basins and several other harbors. In the basins and the areas of heaviest concentrations, source control has lead to decreasing concentrations during the past 10 to 20 years. We know little about long-term trends in sediments of bays and harbors.

However, despite the large historical inputs and locally high sediment concentrations, there is strong evidence that zinc has not contaminated fish or shellfish on a regionwide basis. There is some evidence that zinc has contaminated mussels and several other invertebrates on a local scale, but elevations over levels at reference sites were generally less than a factor of 2 in areas such as the inner channel of Los Angeles and Long Beach harbors.

Current evidence indicates there has been no bioaccumulation of stable anthropogenic zinc in tissues of fish of the Bight, but nuclear weapons' production and testing did result in the presence of radioactive ^{65}Zn in local fish during the 1960s.

Finally, while zinc concentrations in sediments near known sources have declined rapidly in response to source controls, there is no evidence of complimentary decreases in routinely monitored organisms, such as mussels, near these sources. Decreases should not be expected where levels are already normal.

INFORMATION NEEDS

Concern about zinc as a pollutant should probably shift from the open coastal zone to bays and lagoons. Emissions from sewage discharges and fluxes to sediments near boat maintenance facilities and in the deep basins have been declining during the 1970s and 1980s. However, it is evident that no such decline can be confirmed near the heads of bays (for example, Upper Newport Bay) subject to high inputs from storm run-off. It may be advisable to develop new information on automobile activity (tire wear) as an important continuing source of zinc to bays and lagoons. Brush fires may, in the future, be important sources of zinc, through direct aerial fallout as well as from ash run-off. In addition, vessel painting and cleaning facilities should continue to be scrutinized as sources. Coring near vessel works and at the heads of estuaries may be needed to identify buried zinc (and other metal) "hot spots" that may be future sources of contamination if dredged or disturbed. The very low concentrations of zinc in sediments (5 to 20 ppm) at the mouth of the Tijuana estuary (Gersberg et al., 1989) should be scrutinized to see if they represent "background" from bays and lagoons. From an environmental toxicology point of view, it may be informative to determine more about the bioaccumulation and toxicity of zinc in lagoons and adjacent wetland ecosystems receiving highway run-off and in harbor ecosystems where vessel paints and corrosion control devices may be continuing sources of dissolved zinc. The cause of possible zinc depressions in liver of bottomfish in coastal areas may also be important to determine.

CHAPTER 14

POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) are compounds of carbon and hydrogen that consist of two or more benzene rings fused in linear or cluster arrangements (Figure 14.1). They are also referred to as polynuclear aromatics (PNAHs), or polyaromatics. PAHs and the monocyclic (single-ring) aromatic hydrocarbons (MAHs), such as benzene, are collectively known as aromatic hydrocarbons. Aromatic hydrocarbons are only one of several groups of hydrocarbons found in fossil fuels (petroleum, coal) and their refined or combustion products. Other classes of hydrocarbons include aliphatic hydrocarbons (including alkanes, alkenes, and alkynes) and a wide variety of compounds that also contain sulfur, nitrogen and/or oxygen. Presence of these other hydrocarbons can help identify possible sources of associated PAHs.

Concern about PAH levels in the environment stems from the fact that many are potent carcinogens or mutagens. Of the EPA's 129 Priority Pollutants, 16 are PAHs. Reports of cancers in humans from occupationally related PAH exposure date back to 1775 when a London surgeon observed cancers in chimney sweeps (Pott, 1963). By the early 1900s, it was widely recognized that soot (from inefficient combustion of coal), coal tar (a distillate of coal), and coal pitch (the distillate residue) are all carcinogenic to man (Dipple, 1985). Skin, respiratory, and gastrointestinal tumors have been associated with occupational exposure to PAHs (Dipple, 1985). Shimkin et al. (1951) induced skin tumors in mice with extracts of barnacles taken from the entrance to Newport Bay. They isolated 2,3 benzopyrene from the barnacles and considered it the causative agent.

Some PAHs are ubiquitous in nature, while others are more indicative of fossil fuel combustion or petroleum discharges. In Buzzards Bay, Massachusetts for example, several PAHs from combustion (fluoranthene and pyrene) increased significantly in sediment layers deposited between 1850 and 1900 (Hites et al., 1977). Dipple, 1985, estimated the annual United States emissions of B(a)p alone to be about 1000 tons. Approximately 37 percent of this is from heat and power generation, 44 percent from open burning, 17 percent from coke production, and 2 percent from automobile emissions. In contrast, lighter molecular-weight compounds, such as naphthalene and phenanthrene, are the major PAHs detected in water when crude or refined oils are released (Anderson et al., 1974; Lee, 1977). Both naphthalene and phenanthrene readily methylate in water and the resulting alkylated forms are usually more toxic to aquatic biota than the parent compounds. The ratio of naphthalenes and phenanthrenes to total PAH (tPAH) residue, the fossil fuel pollution index (FFPI), has been used as a guide to indicate the degree of PAH contamination by petroleum products versus other sources.

PAHs are metabolized in higher organisms by oxidation of the parent compounds to reactive, water-soluble epoxides. These metabolites are often more toxic than parent compounds. They can be rendered nontoxic by conjugation with glutathione, a naturally occurring peptide. However, reactive metabolites such as epoxides are also free to damage essential proteins and enzymes, as well as DNA. Parent PAH compounds that possess a "bay region" (Figures 14.1 and 14.2) are known to be more reactive to biologically damaging epoxides than those without a bay region (Lehr et al., 1985).

In the marine environment, PAHs, especially higher molecular-weight compounds, adsorb to particulates (Lee, 1977). Sediment and water-column microbes can degrade PAHs, but the higher molecular-weight compounds are acted upon slowly (Eganhouse and Gossett, in press). Mammals, fish, and invertebrates have varying capabilities to metabolize PAHs (Varanasi et al., 1985). Again, higher molecular-weight PAHs are generally not as reactive and tend to bioaccumulate to a greater extent and are retained for longer periods than lower molecular-weight compounds (Konasewich et al., 1982). Fish rapidly metabolize most PAH compounds and excrete them in bile. Therefore, PAHs are not usually detected in fish muscle. However, bivalve mollusks (mussels and oysters) do not rapidly metabolize PAHs. As a result, they are useful indicators of PAH contamination of the marine environment.

Documented sources of PAHs to the Southern California Bight include treated sewage (Eganhouse et al., 1981; SCCWRP, 1988), stormwater run-off (Eganhouse and Kaplan, 1982b; SCCWRP, 1988), and oil spills (Hyland et al., 1989). Poorly documented but suspected sources include aerial fallout and petroleum refinery wastes (Olmez et al., 1991), discharges of drilling fluids and produced waters, natural oil seeps, and hydrothermal seeps.
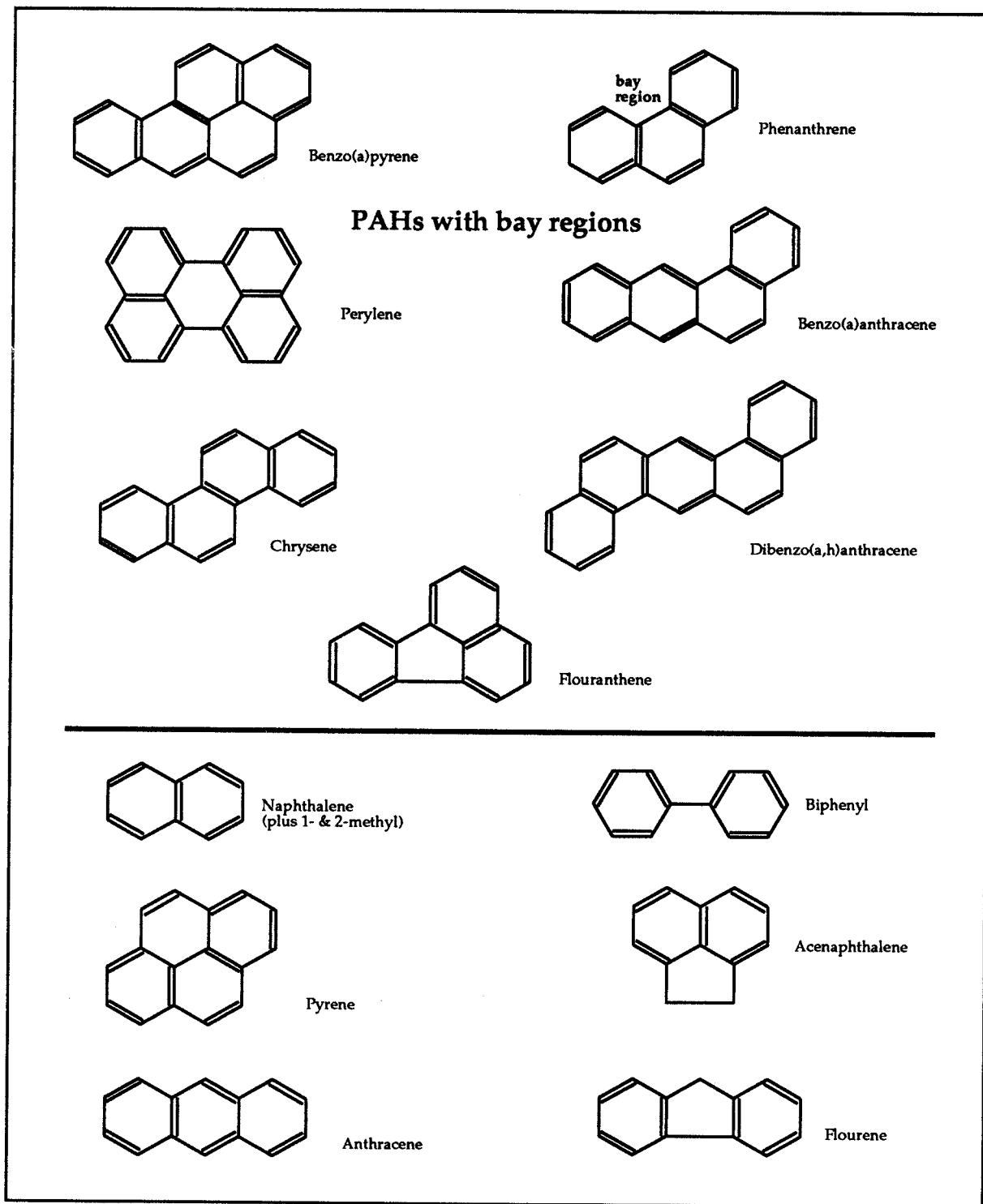
PAHs with bay regions

Benzo(a)pyrene

Phenanthrene

bay region

Perylene

Benzo(a)anthracene

Chrysene

Dibenzo(a,h)anthracene

Flouranthene

Naphthalene
(plus 1- & 2-methyl)

Biphenyl

Pyrene

Acenaphthalene

Anthracene

Flourene

Figure 14.1. California surveys. These 13 compounds, plus 2 alkylated naphthalenes, were common to four data sets used to examine geographic distributions (Figure 14.3).
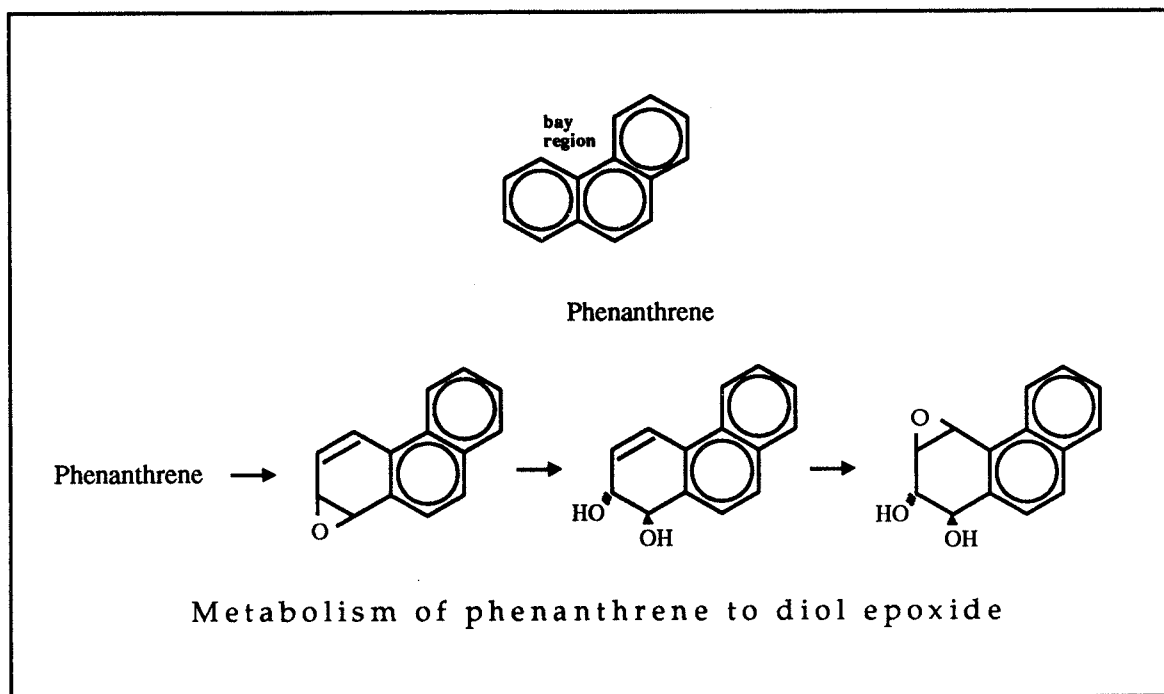
Figure 14.2. Location of "bay region" and related epoxide metabolism of phenanthrene.

Apparently no one has attempted to compare quantities of PAH inputs from various sources. As summarized in Table 14.1, for Santa Barbara and the Los Angeles-Orange County area and described in more detail below, past inputs from ocean dumping (refinery and drilling wastes) could have dominated during the 1960s. Today, run-off and sewage are of primary importance, and oil spills and natural oil seeps are of secondary importance.

Table 14.1. Estimates of annual PAH inputs (mt and percentage) to the Southern California Bight during two periods. Methods and assumptions described in text. Inputs to San Diego Harbor, San Diego area, and Baja California not estimated except as noted in text.

| Source | Time Period | | | |
| | 1960s-1970s | | Mid-1980s | |
	metric tons	percent of total	metric tons	percent of total
Municipal sewage [1]	200-300	23-30	150	28-36
Run-off	200-300	23-30	200 - 300	47-56
Ocean dumping [2]	200-600	30-47	0	00
Major oil spills	50	4-7	50	12
Oil seeps [3]	26-36	3-4	26-36	6-7
Industrial discharges	----------------No estimate available----------------			
Atmospheric fallout (direct)	----------------No estimate available----------------			

[1] Four largest discharges in Los Angeles and Orange counties.
[2] Mid-1960s only.
[3] Coal Oil Point only.

Prior to the 1980s, treated sewage may have been a dominant source of PAHs to the Bight with emissions about 200 mt per year. PAHs have only been measured at useful detection limits (0.05 ppb) in sewage on a few occasions. Based on a sample collected in October 1979, SCCWRP (Eganhouse and Kaplan, 1982a) estimated an emission rate of 110 mt per year of tPAH in the final effluent of the CSDLAC treatment plant. In 1979, the four largest sewage treatment plants discharged 7840 mt of total aromatic hydrocarbons, of which tPAHs was an unknown fraction (Eganhouse and Kaplan, 1981). The CSDLAC treatment plant at Whites Point discharged about 45 percent of this amount of *total aromatic hydrocarbons* (3520 mt per year). If the other treatment plants discharged the same ratio of PAHs to total aromatic hydrocarbons (3%), then the total discharge of PAHs from sewage would have been 244 mt per year in 1979 (200 to 300 mt per year in Table 14.1).

A similar level of information and uncertainty exists for PAH inputs from river run-off. Eganhouse and Kaplan (1982a) estimated that the Los Angeles River discharged 311 mt per year of *total aromatic hydrocarbons*, some fraction of which was PAHs. For a storm event in September 1986, SCCWRP (1988) estimated that the Los Angeles River discharged 0.4 mt per day of PAHs into the Long Beach Harbor area. This is half the yearly estimate of *total aromatic hydrocarbons*, made by Eganhouse and Kaplan (1982a). This suggests that PAHs might compose half (150 mt per year) of the total aromatic hydrocarbons in run-off from that river. Of five rivers sampled during the 1986 storm, the highest PAH emission (78%) was from the Los Angeles River (at Willow Street, 400 kg), followed by Ballona Creek (into Santa Monica Bay, 110 kg or 21%), and the San Gabriel River (near Seal Beach, 4 kg or 1% (SCCWRP, 1988). Trivial PAH inputs were measured from the Santa Clara River (0.018 kg) and Calleguas Creek (0.0056 kg) in Ventura County (but flows were also trivial). If these PAH inputs are extrapolated over a year in which the Los Angeles River might discharge 150 mt, the tPAH input from the five inflows is 192 mt per year. Including many other unmeasured run-off channels in southern California and Baja California, annual PAH inputs from these sources may be in the range of 200 to 300 mt. This is in the same range as inputs from sewage (244 mt per year based on 1979 data).

Additional evidence suggests that the PAH input from stormwater run-off might now exceed that from sewage. PAHs are probably included as part of the "oil and grease" fraction routinely measured in sanitation district effluents. During the past two decades, total annual sewage inputs of oil and grease to the Bight decreased 58 percent from 63,500 mt in 1971 to 26,600 mt in 1987 (Schafer, 1989). The 1979 input was 45,500 mt. Thus there has been a 41 percent reduction between 1979 and 1987. If sewage inputs of PAH decreased proportionately, then 1987 PAH inputs from sewage may have been 144 mt (represented as 150 mt in Table 14.1). If inputs from storm run-off (200 to 300 mt) have not decreased, they now may exceed those from sewage.

Wastes from oil drilling operations, refineries, and chemical plants were discharged to the San Pedro Basin through ocean dumping before 1971, and probably contained PAHs. Approximately 480,000 mt of petroleum refining wastes were dumped between 1946 and 1971 (SCCWRP, 1973). Assuming a PAH concentration of 1 percent, the tPAH input to the basin from this source may have been 4800 mt, or 192 mt per year. This is equivalent to the current input from sewage or run-off. Further, more than 3 million mt of oil drilling mud and cuttings were dumped into the San Pedro Channel between 1966 and 1970, when such dumping was prohibited (SCCWRP, 1973). The PAH concentration of drilling muds is not known. If the concentration was between 0.01 to 0.1 percent by weight, then the total 1966-70 input from dumping might have been about 300 to 3000 mt (60 to 600 mt per year) over the 5-year period. Thus, dumping may have been the dominant input during the 1960s.

There is little data available from which to judge the magnitude of sources other than sewage or stormwater run-off. There have been numerous small spills of fuel and other petroleum products (that may contain PAHs) in all harbors and coastal waters of the Bight. For the period 1973 to 1975, Bright (1979) estimated there were about 34 spills per 100 vessel port calls including about 8 spills of more than 50 gallons per 1000 port calls. Very large spills have been infrequent (one every 10 years), but notable. They include: the Tampico Maru which spilled 2.48 million gallons of No. 2 diesel fuel near Punta San Isidro (Erendira), Baja California in 1957 (North, 1967); the blowout at Platform A in the Santa Barbara Channel in 1969 which discharged 3.25 million gallons of crude oil (Straughn, 1979); the Plan de Ayala which spilled 2.52 million gallons (presumably Bunker C fuel oil) near Rosarito, Baja California, in April 1971 (Salas-Flores *et al.*, 1975); the tanker Sansinena that exploded in Los Angeles Harbor spilling 0.9 to 1.3

million gallons of Bunker C oil (Soule *et al.*, 1978); and the sinking of the Pacific Baroness near Point Conception in 1987 which may have released a total of 0.38 million gallons of No. 2, 3, and 4 fuel and lubricating oils, the only spill for which PAH contamination was confirmed (Hyland *et al.*, 1989). Inland spills may also lead to hydrocarbon and PAH inputs to inshore areas. One such spill of 5000 to 7000 gallons of crude oil occurred at Prado Dam on the Santa Ana River in 1983 (Kemerer *et al.*, 1985).

Several assumptions are needed to estimate the possible input of PAHs from these large spills (Table 14.2). PAH concentrations by weight, range from about 1 percent in crude oils, 4 percent in Bunker C oil, and 9 percent in No. 2 diesel oil (NRC, 1985). Using the computational assumptions listed in Table 14.2, then the amount (by weight) of tPAHs introduced by these spills was about 735 mt for the 1957 Tampico Maru (diesel) spill, 366 mt for the 1971 Plan de Ayala spill, 131 to 189 mt for the 1977 Sansinena (Bunker C) spill, 130 mt for the 1987 Pacific Baroness (diesel) spill, and 110 mt for the 1969 Santa Barbara (crude oil) discharge. Together, PAH input to the Bight from these spills was 1472 to 1530 mt over the 30-year period 1957-87. On an annual basis, this is equivalent to a spill input of about 50 mt per year. Depending on assumptions made about other sources, major spills may have contributed from 7 to 12 percent of total inputs on an annual basis (Table 14.1). Of course these spills and the sewage and run-off inputs have been in widely scattered locations and did not necessarily contribute to a common regionwide pool. However, geographically, combined inputs to the Los Angeles County coastline might be an order of magnitude higher than the same kinds of sources (sewage, run-off, and spills) to more distant areas (for example, Santa Barbara and Baja California).

Table 14.2. Description of five large oil spills in the Southern California Bight with estimates of amounts of PAHs released.

	Tampico Maru [1]	Platform A [2]	Plan de Ayala [3]	Sansinena [4]	Pacific Baroness
Date:	March 1957	January 1969	April 1971	December 1976	September 1987
Location:	Near Erendira Baja California	Santa Barbara, California	Rosarito, Baja California	Los Angeles Harbor, California	Near Point Conception
Type:	No. 2 Diesel Diesel oils	Crude oil	Bunker C fuel oil		Bunker C fuel oil
Amount:					
10^6 gal	2.48	3.25	2.52	0.9 - 1.3	0.38
10^6 L	9.39	12.30	9.54	3.41 - 4.92	1.44
Specific Gravity (assumed):	0.87	0.89	0.96	0.96	0.87
Amount:					
10^3 tons	8.17	10.95	9.16	3.27 - 4.72	1.25
% PAH (assumed)	9	1	4	4	9
Amount:					
PAH mt	735	110	366	131 - 189	130

[1]North, 1961; North, 1967; Mitchell *et al.*, 1970
[2]Nicholson, 1972 and others
[3]Salas-Flores *et al.*, 1975
[4]Soule, 1980
[5]Hyland *et al.*, 1989

Oil spills (from ships and shore) may have been major sources of PAHs in the decades preceding the 1960s. Chronic oil pollution was recognized as a serious environmental problem 70 years ago in California (Anon., 1917). As oil fields developed southward from central California; so did spills and leakage from unregulated new fields along the coast such as at San Luis Obispo, nearby at Pismo Beach, and Oceano in 1918, 1919, and 1920 (Duke, 1918; Thompson, 1920). Spills and releases from gas houses, oil refineries, and tankers were common by the mid-1920s (Anon., 1922; Anon., 1923). Following passage of federal legislation in 1925, the California Department of Fish and Game began a major effort to reduce releases, citing specific spill incidents and fish kills in the Ventura River (Anon., 1926), Long Beach Harbor (Anon., 1927a), and Alamitos Bay (Anon. 1927b). By 1927, Los Angeles was the largest shipping point for oil in the world (Anon., 1927c). Effort shifted to Orange County in 1928 in attempts to stop spillages at Huntington Beach and Newport Bay. Nevertheless, spills continued. There was a 600-barrel release that covered at least 9 miles of Ventura County beach in 1929 (Anon., 1929b) and a 350-barrel release at San Pedro (Anon., 1932a). Sump farms and other controls were established to reduce flows into

Domiguez Channel in Los Angeles Harbor. By the early 1930s, spills from offshore ships were considered a greater menace than shoreline leakages (Anon., 1929a; Anon., 1932b). Oil spills were apparently responsible for damaging native oyster beds in Alamitos Bay and Tijuana estuary and contributed to poor water quality of San Diego Harbor (Bonnot, 1935). Refineries were allowed to discharge wastewater directly into Los Angeles-Long Beach harbors until 1968 (Reish, 1971; 1978). Thus, PAHs have probably been entering harbors and marinas since rapid growth of coastal petroleum development began following the turn of the century.

PAHs may have been discharged in Baja California during the 1960s and 1970s as a result of observed and suspected spills of fuel oil associated with offloading tankers at a power plant near Rosarito, north of Ensenada. Vanadium and nickel concentrations and ratios lead Salas-Flores *et al.* (1975) to conclude that oil contamination was chronic in that area but sources could not be positively identified. Thus it would not be surprising to find elevated concentrations of PAHs in mussels or sediments from this area.

Although the PAH content of crude oil is low (1 %), PAH inputs may also come from the many active oil seeps along the southern California coast, such as at Coal Oil Point (Spies *et al.*, 1980) and Redondo Submarine Canyon in Santa Monica Bay. The Coal Oil Point seeps discharge 50 to 70 barrels (or 2100 to 2940 gallons per day) of crude oil. This amounts to 0.77 to 1.07 million gallons of oil per year. The PAH input might be about 26 to 36 tons per year. Thus, the PAH input from this seep may be about 5 to 6 percent of the total anthropogenic PAH input described above (run-off, sewage, and spills); while small, this could be locally important and indicates a need to estimate PAH inputs from all seeps.

The composition of PAHs from different sources can vary greatly. Most of the PAHs in the Los Angeles River entered from the urbanized basin itself and did not come from mountain run-off (SCCWRP, 1988). The dominant PAHs in both sewage and stormwater run-off include naphthalene and its substituted compounds and phenanthrene/anthrarene. Emissions of higher molecular weight PAHs (such as the carcinogen B(a)p) were minor (SCCWRP, 1988). Finally, the composition of PAHs and other hydrocarbons in urban run-off and sewage effluent led Eganhouse *et al.* (1981) and Eganhouse and Kaplan (1982a) to conclude that these compounds originated mainly from petroleum products, not from combustion sources or crude oil seepage or spills. Nonetheless, Payne *et al.* (1979) reviewed evidence arguing that combustion products (fire fallout and urban air particulates), contain far more mutagenic and carcinogenic PAHs than do crude oil and petroleum products. Crankcase oil, a major source of petroleum hydrocarbons in run-off, was clearly mutagenic, but the mutagenic agents were not benzopyrene or benzoanthracene as expected (Payne *et al.*, 1979).

Based on dated core studies (Venkatesan *et al.*, 1980), there is evidence that aromatic hydrocarbon inputs to the San Pedro Basin peaked in 1966 through 1968 and have since been declining (see below and Figure 14.3). The slowly rising concentrations between 1917 and 1962 are inconsistent with anecdotal data on the rise and fall of onshore inputs from oil fields in the 1920s and 1930s; but are consistent with the known history of potential inputs from ocean dumping of refinery wastes (1945-71) and drilling muds (1966-70) in this basin. This trend is commensurate with cessation of dumping and decreases of oil and grease from combined sewage discharges that declined 58 percent between 1971 and 1987 (SCCWRP, 1988). However, actual trends for PAHs are unmeasured and unknown.
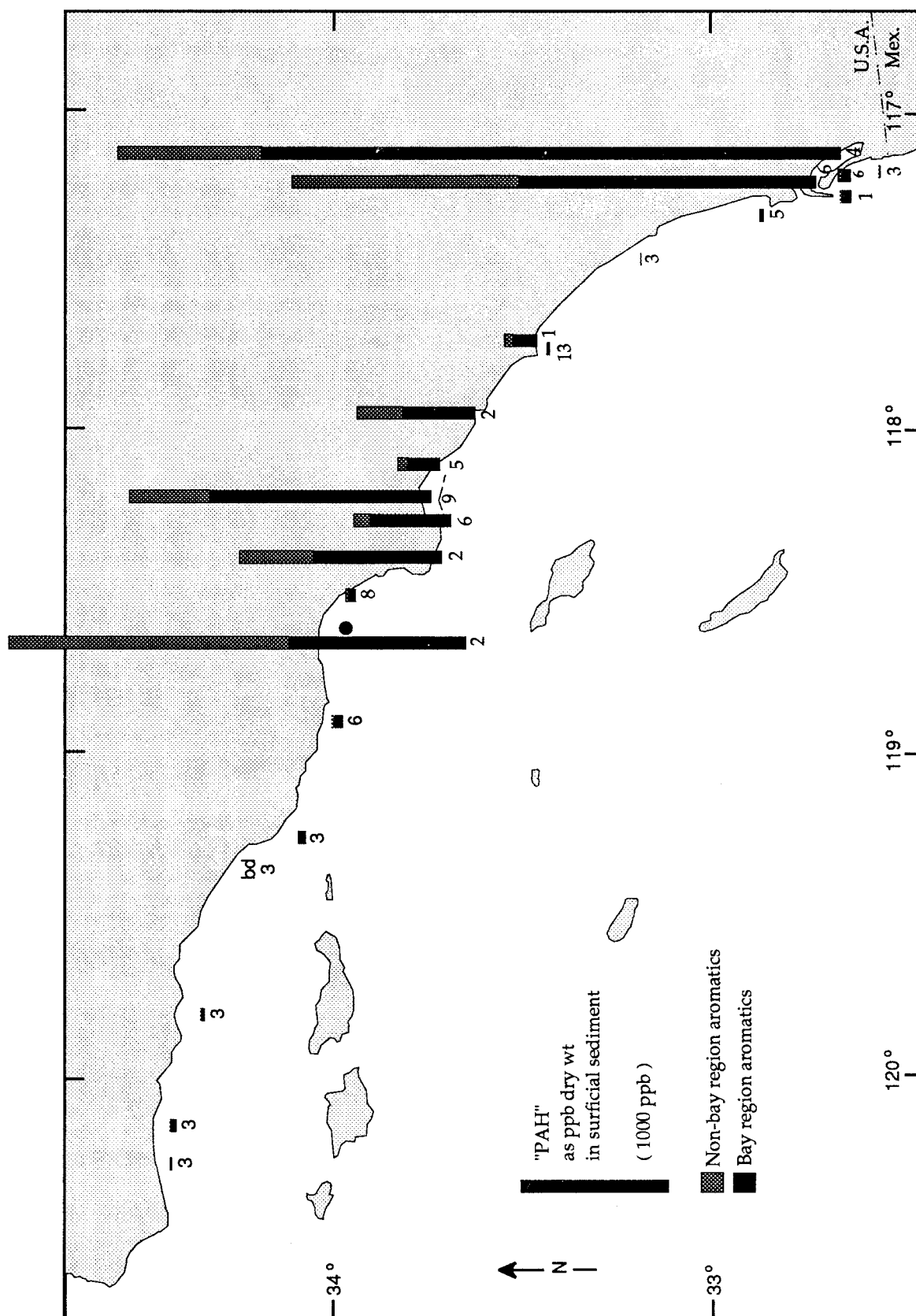
Figure 4.3 Relative total PAHs in surficial sediments in ppb dry weight, 1984-86.

There have been dramatic local and regional gradients of PAH concentrations in sediments of the Southern California Bight such that the area contains both the cleanest and among the most contaminated sites in the United States. However, a considerable amount of data manipulation was required to arrive at this observation because each survey or monitoring program has measured a different mix of compounds at different sites, depths, and proximities to point sources.

Broad-scan sampling of individual PAH compounds in sediments of the Bight has occurred only since the mid-1980s. To evaluate the distribution of tPAH concentrations, it was necessary to critically review available reports, exclude those that only measured one or a few compounds, and reduce the remaining data sets to a suite of common compounds (Figure 14.1). Nine data sets were encountered which analyzed for one or more of the 18 PAH compounds measured in sediments by the NOAA NS&T Program. Four were not used due to their limited number of analytes: Orr and Grady (1967) and Aizenshtat (1973) measured only perylene; Gossett *et al.* (1983a) included only naphthalene; and only half of the NS&T analytes were in common with those of Swartz *et al.* (1985) or Risebrough (1987). The data by Anderson *et al.* (1988) is discussed in the text but not included in Figure 14.3. Three other references, which reported sampling between 1984 and 1986, were selected for presentation with NS&T data: Malins *et al.*, 1986a; Thompson *et al.*, 1987; and Anderson and Gossett, 1986 (Table 14.3).

Table 14.3. Brief description of five survey activities producing data on PAHs in sediments from the Southern California Bight, 1984 through 1987.

Author	Number of Marine Sites	Number of PAH compounds	Year(s)	Range, total PAHs (ppb dw)
Malins *et al.*, 1986a	6	12	1984	54 - 2800
Thompson *et al.*, 1987	39	28	1985	<4 - 149
Anderson and Gossett, 1986	21	43	1986	142 - 15,470
Anderson *et al.*, 1988	11	26	1987	<3 - 20,387
NOAA, 1988[1]	18	18	1984-87	nd - 8626

[1] Range of station averages; normalized to fine grain fraction.

Malins *et al.* (1986a) measured 12 PAH compounds in sediments collected in December 1984 from three stations in Los Angeles-Long Beach harbors and three sites outside the harbors (Whites Point, Santa Monica Bay, and Dana Point). All 12 PAHs were also measured by NS&T, with detection limits ranging from 2 to 4 ppb dw. Total concentrations of the 12 compounds ranged from 54 ppb dw offshore of Dana Point to 2800 ppb dw at Queensway Beach in Long Beach Harbor.

Thompson *et al.* (1987) measured 28 PAH compounds in sediments collected in 1985 from three stations at each of 13 remote (non-urban areas) coastal shelf transects, thus providing a potentially powerful reference area data set. Transect stations were located along the 30-, 60-, and 150-meter isobaths mainly off Santa Barbara, Ventura, and San Diego counties. Detection limits ranged over an order of magnitude for any given PAH compound, with limits varying from 1 to 93 ppb dw. Of the 28 compounds analyzed, 21 were below detection limits in all sediment samples. For presentation here, data from all three depths have been composited for a site mean.

Anderson and Gossett (1986) measured 43 PAH compounds (29 groups) in triplicate sediment samples from 21 marine sites located between control Santa Monica Bay and southern San Diego Harbor and at 3 inland river sites during the spring of 1986. The marine sites were mainly nearshore (depth range less than 1 to 154 meters; median, 6 meters) and in harbors, bay, and river mouths. Detection limits of individual compounds generally ranged from 1 to 20 ppb dw.

For the presentation in Figure 14.4, 15 of the 18 NS&T PAH compounds (8 low molecular weight (LMW), 7 high molecular weight (HMW)) were chosen to represent tPAHs (Figure 14.1). PAHs sampled by NS&T also include benzo(e)pyrene, 2-6-dimethylnaphthalene, and 1-methylphenanthrene. Due to incomplete documentation of detection limits, zeros were used in calculations for any analyte that was reported as below detection. The final "total" in some instances represents only half of the PAH residues reported by the original investigators, yet allows for comparison among the different studies. In addition, data were differentiated between those aromatics that possess a "bay region" and those which do not (Figures 14.1 and 14.2).

As summarized in Figure 14.4, concentrations of tPAH ranged over 4 orders of magnitude from below detection in open coast areas to over 9000 ppb dw at a site in north San Diego Harbor. Highest values (more than 1000 ppb dw) occurred in San Diego and Los Angeles harbors, near the abandoned Hyperion sludge outfall in Santa Monica Bay, and near the Whites Point outfall at Palos Verdes. In the survey conducted by Anderson and Gossett (1986), concentrations of tPAH at the marine sites ranged from 142 ppb dw at a 60-m deep site off San Mateo Point, northern San Diego County, to 15,470 ppb dw in the East Turning Basin of Long Beach Harbor. Three sites along the east shore of San Diego Harbor produced high levels of tPAH (5459 to 12,802 ppb dw) as did two river entrances (Los Angeles, 8599 ppb dw and San Gabriel, 3242 ppb dw), and three ocean outfall sites (off Whites Point, 7402 ppb dw; at the now-abandoned 7-mile sludge outfall site, 11,317 ppb dw; and at the diffuser of the Orange County outfall, 3528 ppb dw). Two other sewage outfall sites and one refinery effluent discharge site had very low concentrations (Point Loma, 154 ppb; Santa Monica 5-mile, 393 ppb; and the Chevron facility at Playa del Rey in Santa Monica Bay, 218 ppb dw).

Residues from open coastal areas were consistently lower than those from embayments or outfall areas. This was particularly true in the SCCWRP 1985 Reference Survey (Thompson et al., 1987; Figure 14.4) for the 150-km Santa Barbara-Ventura mainland shelf. The average tPAH concentrations ranged from below detection to 149 ppb dw for the 100-km of coastline from Dana Point (southern Orange County) to Point Loma (San Diego County). In these regions, the overall average concentration was below total detection limits of about 20 ppb. Further, no LMW PAHs, and only several of the HMW PAHs were found. The assemblage of PAHs encountered also varied. The index of fossil fuel PAHs (naphthalenes and phenanthrenes) to tPAHs (FFPI) indicates proportionally greater contamination by PAHs associated with fuel off San Diego Harbor, along Orange County, and at the Santa Monica Bay outfall (Figure 14.5). Otherwise, where tPAH was low, it was dominated by the more persistent, high-weight, bay region compounds characteristic of combustion sources.
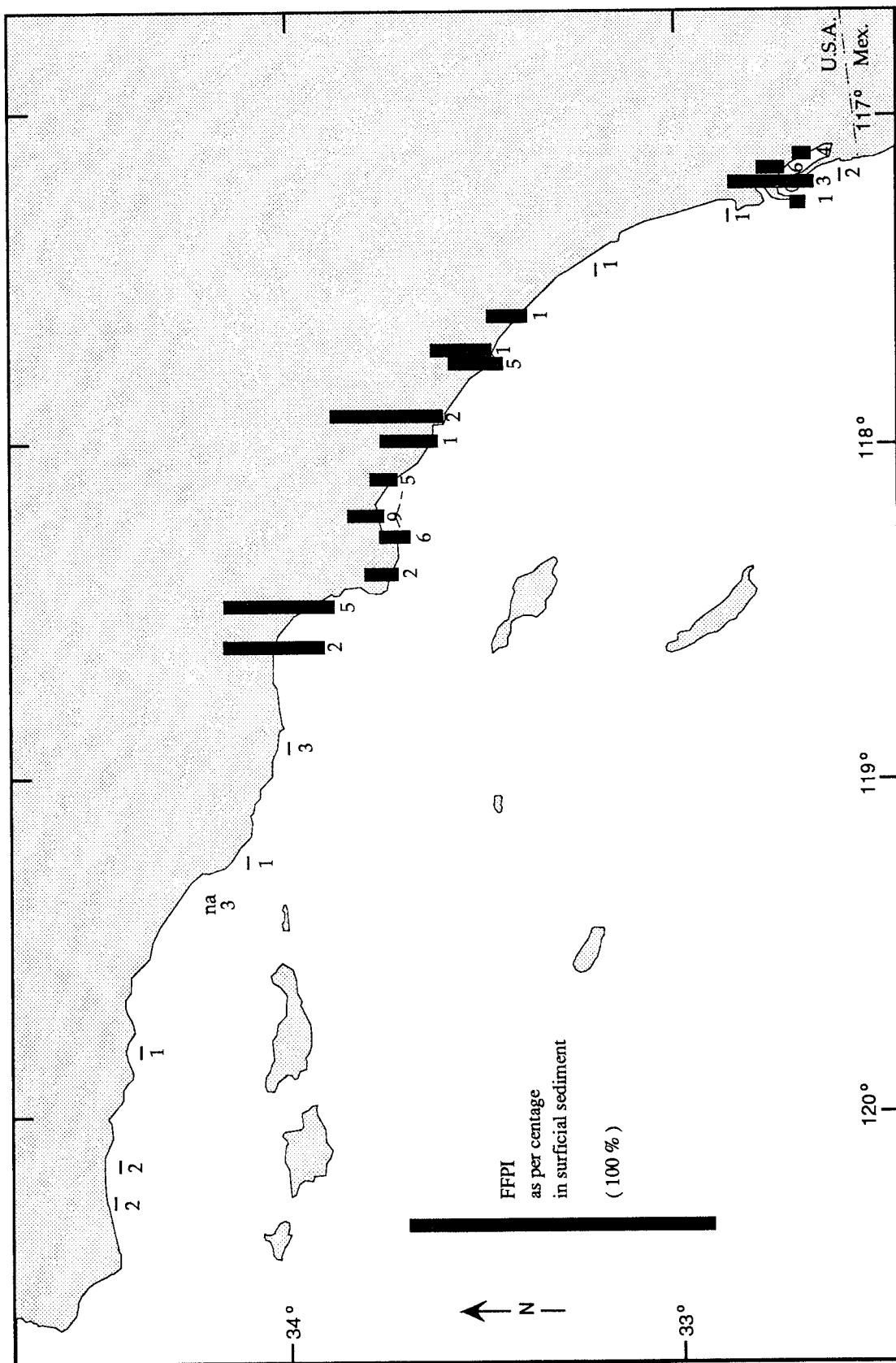
Figure 14.4. Fossil Fuel Pollution Index (FFPI) of surficial sediments in percent, 1984-86 (composited from date in Figure 14.3).
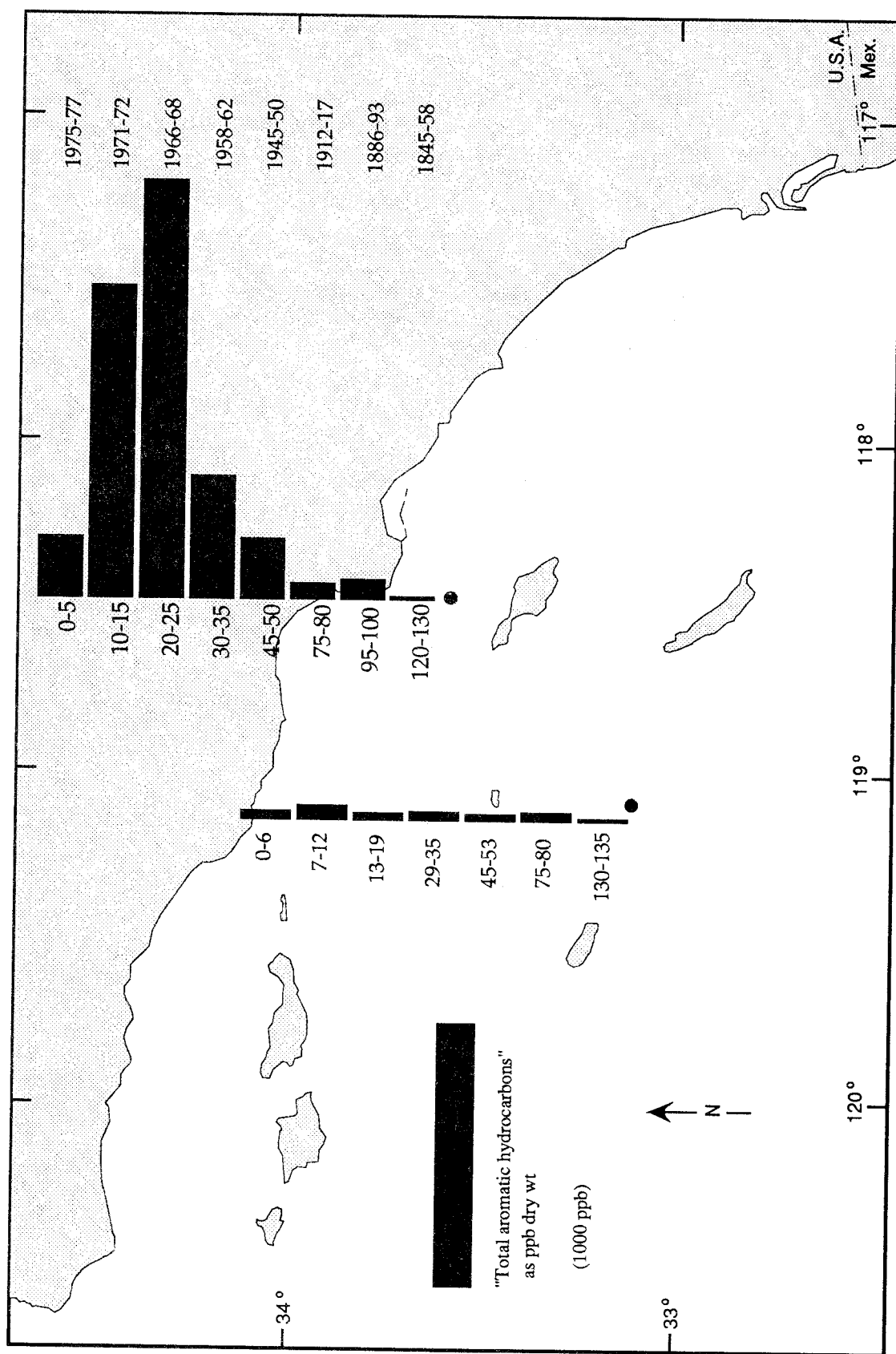
Figure 14.5. Total aromatic hydrocarbons in sediment core samples, as ppb dry weight. Values represent an undifferentiated total, as reported by Venkatesan (1980).

14-12

A few areas of the Bight have been sampled well enough to resolve local gradients of PAHs in sediments. These include San Diego Bay and San Diego Harbor where six sites were surveyed as part of the 1987 NOAA NS&T Benthic Surveillance Project. Total average PAH concentrations reported by McCain *et al* (1989) ranged from 100 ppb dw at a site outside the harbor entrance (off Coronado) to 4000 ppb dw at a site just south of the Coronado Bridge (Tables 14.4 and 14.5). Another well-sampled area surrounds the site of the wreck of the Pacific Baroness, 430-m deep and 19 miles southwest of Point Conception. The vessel sank in September 1987. In November 1987, tPAHs averaged 27,222 ppb dw (range 12 to 139,000) against a local background of 10 ppb dw and a regional background of 83 ± 30 ppb dw (Hyland *et al.*, 1989; Table 14.6)

Table 14.4. Summary of tPAH concentrations in sediments at Dana Point and at six San Diego Bay and Harbor sites sampled during the 1987 NOAA NS&T Benthic Surveillance Project. Data from McCain *et al.*, 1989, converted from ppm to ppb.

Site	Total PAH ppb dw mean		standard deviation
Dana Point	≤20		
Outside San Diego Harbor	100	±	200
Shelter Island - San Diego Harbor	400	±	300
West Harbor Island - San Diego Harbor	800	±	600
North Bay (city) - San Diego Harbor	2800	±	1100
South Bay (south of Coronado Bridge) - San Diego Harbor	4000	±	3400
National City	1500	±	1000

See Table 14.5 for a list of compounds included.

Table 14.5. PAH compounds analyzed by the NS&T Program.

LOW MOLECULAR WEIGHT
napthalene
2-methylnaphthalene
1-methylnaphthalene
biphenyl
2,6-dimethylnaphthalene
acenaphthene
1-methylphenanthrene

HIGH MOLECULAR WEIGHT
fluoranthene
pyrene
benz(a)anthracene
chrysene
benzo(e)pyrene
benzo(a)pyrene
perylene
dibenz(a,h)anthracene

Table 14.6. Total PAH concentrations (ppb dw) in surface sediments from the <u>Pacific Baroness</u> shipwreck site (430 m deep, 19 km SW Point Conception (November 1987)) and for other regional data collected as part of the MMS California OCS Monitoring Program. From Hyland *et al.,* 1989. See reports cited in Hyland *et al.* for details.

Sampling Area	Total PAH Mean	±	Standard Deviation (or Range)
Regional Background	83	±	30
Wreck site control [1]	10	±	3
Hidalgo oil platform area	128	±	100
Wreck site grid [2]	27,222	±	49,682 (12 - 139,000)
Ship oil	8,700,000		

[1] 8 km to the NW of the wreck

[2] 500 m radius around wreck

Off central Orange County (Huntington Beach), 20 PAHs were measured in triplicate samples from 13 stations along the 60-m isobath for several kilometers on either side of the CSDOC ocean outfall. Samples were taken quarterly beginning in August 1985 (CSDOC, 1987; 1988). The detection limit for most compounds was 20 ppb dw, but there were several at 40 ppb and one at 400 ppb dw. Data were reviewed for eight quarters (August 1985 to April 1987). Concentrations of total (20) PAHs ranged from below detection in most samples to 6400 ppb dw in one sample taken from the zone of initial dilution (ZID) adjacent to the outfall. Background concentrations at eight stations 1 km or more from the ZID and several kilometers from Newport submarine canyon, ranged from below detection during two quarters to a maximum of 73 ppb dw in October 1987 (overall mean, 24 ppb dw). Samples from three stations within the ZID ranged from 7 to 6400 ppb dw (overall mean, 1004 ppb dw). However, this was not the only "hot spot." PAHs occurred frequently at a deep (60-m) station at the head of Newport submarine canyon within 1 km of Newport at Balboa fishing pier. Here tPAH concentrations ranged from below detection in October 1985 to 250 ppb dw in October 1986 (overall mean, 78 ppb dw). The most frequently occurring compounds in 312 samples from this entire survey transect are shown in Table 14.7. All maximum concentrations occurred either at the outfall ZID station or in the head of Newport submarine canyon.

Table 14.7. Most frequently occurring PAHs in sediment samples in the CSDOC monitoring area August 1985 to April 1987 (CSDOC, 1987; 1988).

Compound	Percent of samples present (out of 312)	Maximum concentration ppb dw
2-methylnaphthalene	14.1	96
phenanthrene	12.8	3600
napthalene	9.3	32
fluoranthene	6.1	3000
pyrene	3.5	2000
benzo(b)fluoranthene	3.5	200
benzo(a)anthracene	3.2	1700
chrysene	2.6	1900
anthracene	1.9	77
benzo(k)fluoranthene	1.9	1100

The CSDOC quarterly monitoring data, as reported in CSDOC (1986 and 1987) provide evidence that PAH concentrations in sediments of the coastal shelf may vary seasonally. The numbers of compounds (out of 20) occurring above detection fell from 9 to 5 during the summer and fall of 1985, rose to 17 by April of 1986, fell again to 3 in the fall of 1986, and rose again to 12 and 11 in the winter and spring of 1987 (Table 14.8). The highest numbers of compounds (9 and 17) were detected during the wet seasons and the lowest (3 and 5) during the dry seasons; suggesting that winter stormwater run-off may be contributing PAH inputs to the shelf. Data were not available to compute trends in tPAH concentrations.

Table 14.8. Number (out of 20) of individual PAH compounds occurring above detection limits in sediments from 13 sites sampled along the 60-m isobath in eight quarterly surveys off northern Orange County, 1985 through 1987 (CSDOC, 1986; 1987).

Year	Month	Quarter	Numbers of PAH compounds Above Detection Limits
1985	August	Summer	9
	October	Fall	5
1986	January	Winter	9
	April	Spring	17
	July	Summer	4
	October	Fall	3
1987	January	Winter	12
	April	Spring	11

In the fall of 1987, Anderson et al. (1988) returned to 11 sites sampled in 1986 and measured 26 PAHs. Concentrations ranged from less than 3 ppb dw in Upper Newport Bay to 20,387 ppb dw at the abandoned 7-mile Hyperion sludge outfall in Santa Monica Bay (median 4711 ppb dw). Overall, concentrations at these 11 sites were considerably lower than the range and median encountered in 1986 for the same sites (142 to 15,470 ppb dw, median 7588 ppb dw). The only areas where levels were higher or similar in 1987 were the abandoned 7-mile sludge outfall, the Los Angeles River in Queensway Beach, Long Beach, and the three San Diego Harbor sites between the San Diego Airport and the naval shipyards. The Orange County site, in 1987, produced a tPAH concentration of only 90 ppb dw (compared to 3528 ppb in 1986).

Sediments of the southern California mainland shelf are among the cleanest as well as most contaminated in the United States with respect to PAHs. NOAA (1988) compiled data on tPAHs (18 compounds) in sediments from 177 sites sampled during the 1984-85 NS&T Benthic Surveillance Program surveys and the 1986-87 Mussel Watch surveys. Concentrations were normalized to fine grain material (and are therefore higher than for non-normalized data). They were normalized by dividing concentrations by percent fine material. Only sites with greater than 20 percent fine-grained material were normalized. The median normalized concentration for means from 177 U.S. sites was 687 ppb dw with a range for detected values of 2 ppb dw for a site at Oceanside, California to 57,778 ppb dw at a site in Boston Harbor, Massachusetts. The median for the 18 sites in southern California was 1162 ppb dw or about double the national median of 687 ppb dw. Concentrations for the southern California sites ranged from "not detected" at Point Loma and La Jolla, to 8626 ppb dw at a site in San Diego Harbor near Harbor Island. The total normalized PAH concentration at this single site in San Diego Harbor ranked among the 20 highest concentrations nationwide (NOAA, 1988). However, sediments just outside this harbor and northward 100 km to Dana Point (the San Diego-southern Orange County coastline) were the least contaminated sites nationally (range 0 to 3 ppb). By contrast, sediments of the entire northeast coast from Sears Island, Maine to a site in Delaware Bay contain total normalized PAHs in the range 1478 to 57,800 ppb, with an overall median of 5970 ppb, or about 10 times the national median.

The overall non-normalized mean level of tPAH in sediment measured by NOAA's NS&T Program between 1984 and 1989 was 1341.9 ppb dw (median 312.67 ppb dw)

It is clear from the data reviewed above that PAHs are natural components of shelf sediments but not in the ranges experienced in San Diego Harbor and near Los Angeles. This appears to be true even near chronic petroleum seeps and sites of crude oil spills such as the heavily oiled Santa Barbara shelf. Thus, "background" concentrations of tPAHs are probably those measured in the cleaner areas, in the range of 1 to 100 ppb. However, higher concentrations can occur naturally elsewhere. Near hydrothermal vents in the Guaymas Basin, Gulf of California, for example, total concentrations of 26 PAHs (from high temperature pyrolysis of petroleum) were 578 and 824 ppb dw (Simoneit and Lonsdale, 1982). In cores from a Gulf of Mexico oil seep natural concentrations ranged from 177 to 6,800 ppb dw (Wade *et al.*, 1989).
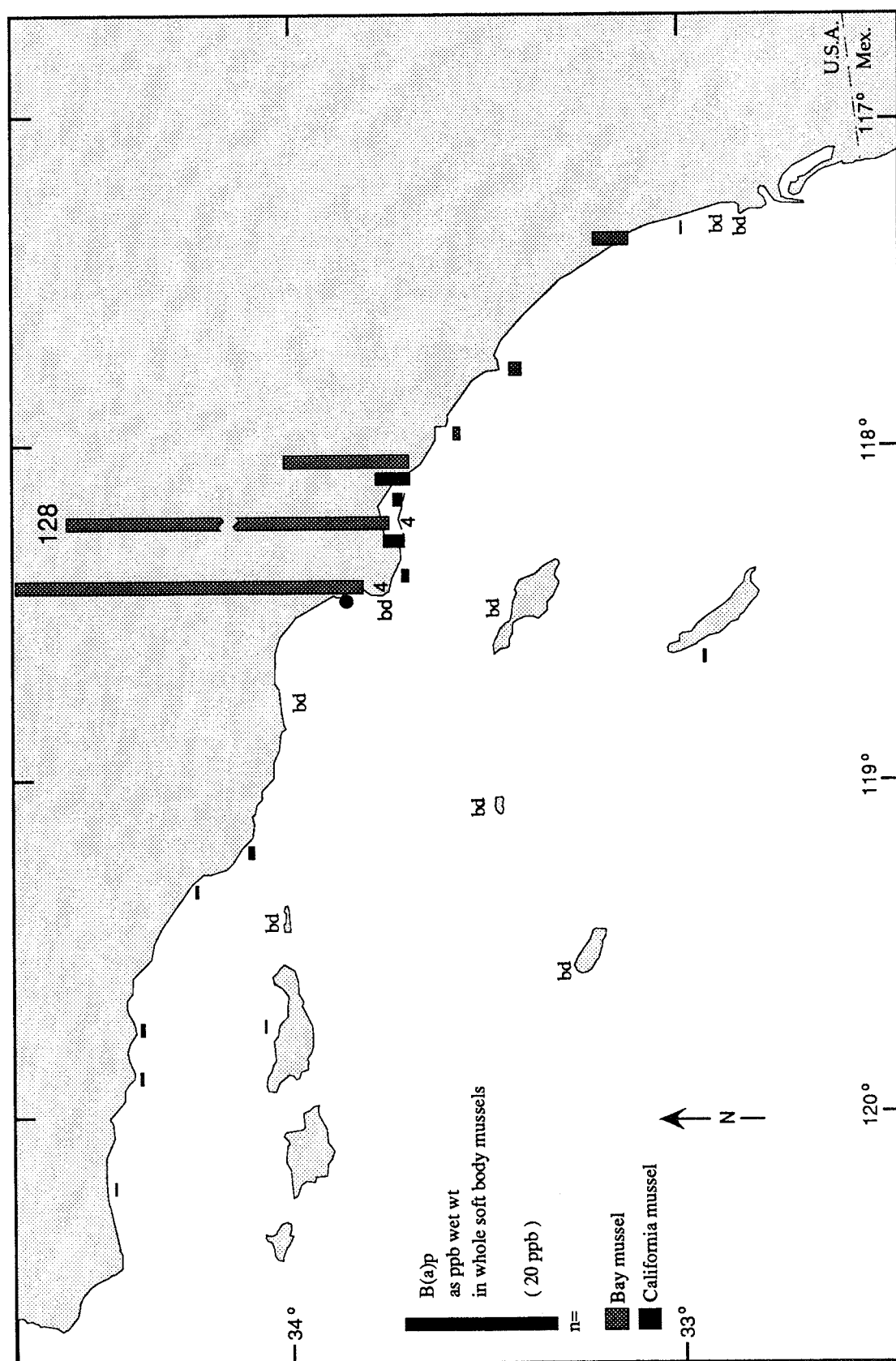
Concentrations of tPAHs that have been associated with detrimental biological effects from sediment exposures have ranged from 0.0009 to 21,200,000 ppb dry weight (Long and Morgan, 1990). Total PAHs most often included the sum of 13 to 18 individual compounds, although some studies summed as few as 4 or as many as 21 compounds. The lower 10th percentile of concentrations associated with detrimental effects (ER-L) was determined to be 4000 ppb (Long and Morgan, 1990). The 50th percentile of concentrations with associated observed effects (ER-M) was 30,000 ppb tPAHs (Long and Morgan, 1990). None of the concentrations of tPAH in southern California sediment encountered in this analysis exceeded 3,5000 ppb. However, sediments from San Diego Harbor, the Pacific Baroness wreck site, Long Beach Harbor, Whites Point, Santa Monica Bay Hyperion outfall site, and the Orange County outfall site have exceeded 4000 ppb tPAH at some time in the past.

Determinations of long-term temporal trends of sediment PAHs are possible only from core surveys. Venkatesan *et al.* (1980) examined sections from sediment cores collected in the San Nicolas and San Pedro basins (Figure 14.5) and reported *total aromatic* hydrocarbons. The San Pedro core was also dated by the ^{210}Pb method. Residues at this basin increased sharply from 10 ppm in the mid-1800s to well over 1600 ppb in approximately 1966 to 1968, and then began to decline. Concentrations in the 1975-77 core segment matched the 1945-50 value of 230 ppb. Levels in a San Nicolas basin core (11 to 49 ppb) site did not appear to change significantly over time, though the maximum concentration (49 ppb dw) was in the 7-12 cm segment (undated). If PAHs collectively or individually followed the patterns of *total* aromatic hydrocarbon in these cores, then the San Pedro basin as well as the mainland shelf may have been contaminated by PAHs from anthropogenic sources (but not the San Nicolas basin). Also, PAH loadings may have decreased about 75 percent between 1966-68 and 1975-77. These hypotheses need testing.

PAHs IN MUSSELS

Use of mussels to monitor PAHs between 1976 and 1986 reveals geographic trends similar to those from sediments.

In addition to NOAA's NS&T Program, two previous studies of PAHs in mussels were available: Dunn and Young, 1976 and Gossett *et al.*, 1982. Both studies measured only one compound--B(a)p. Dunn and Young sampled *M. edulis* at 19 stations during the winter of 1974 (from Bodega Head to San Diego Bay plus six Channel Islands sites). Their sampling sites were chosen to be at least 1 km from piers or point-sources wherever possible. Their detection limit for B(a)p was 0.1 ppb ww. Gossett *et al.* (1982) sampled *M. edulis* and adjacent sediments from four sites within Los Angeles Harbor and four along the Santa Monica Bay shoreline during 1981 with a detection limit for B(a)p of 1 ppb ww. Data for these two studies are presented in Figure 14.6.

Figure 14.6. B(a)p in mussels. Sample size of one, unless stated otherwise. Sources: Dunn and Young, 1976; Gossett et al., 1982.

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Levels of B(a)p in Dunn and Young's samples of *M. edulis* appear to be higher than those in samples of *M. californianus*. However, since these two species were never sampled at exactly the same site, strict comparisons are not possible. Levels were also generally higher in samples collected from pilings as opposed to rocks. These pilings may have been coated with creosote, a known source of PAHs. The highest B(a)p concentration in *M. californianus* was from Seal Beach. A level of 8.2 ppb ww B(a)p was observed in samples of *M. edulis* from pilings, while *M. californianus* from rocks contained 2.3 ppb ww. Intermediate values were observed in samples from other harbor sites; 2.3 ppb at Oceanside, 1.4 ppb at the Long Beach breakwater, and 0.6 ppb at King Harbor (Redondo Beach). Residues were generally low (0.1 to 0.2) along open coastal areas and below detection (less than 0.1 ppb) in samples from the offshore islands. The data of Gossett *et al.* (1982) from a later period than Dunn and Young's samples, yielded high concentrations in *M. edulis* from Los Angeles Harbor (3 to 280 ppb) and Santa Monica Bay areas (10 to 71 ppb). Also, they demonstrated that *M. edulis* had concentrations 10 times higher than those in nearby sediments.

Data for tPAHs from the 1986 NS&T Mussel Watch (NOAA, 1989) are provided in Figure 14.7. In contrast to the earlier data (Figure 14.6), B(a)p was observed in only one sample, from north San Diego Harbor (46 ppb). Total PAHs were generally below detection limits except in or near harbors and at two Channel Island sites. At Bird Rock, Santa Catalina Island, high residues may reflect heavy recreational boating use of Isthmus Cove, residual material from historical dumping offshore, or unreported oil seepage. High levels at the Santa Cruz Island site remain uninterpreted. Concentrations of PAHs in mussels from a Gulf of Mexico oil seep ranged from 26 to 7530 ppb dw (Wade *et al.*, 1989), thus there may be PAHs inputs from unreported seeps in the Channel Island area.

Levels of PAHs in mussels of the Southern California Bight are extremely low compared to mussels and oysters from the rest of the U. S. coastline. NOAA (1989) compiled data, separately, on LMW and HMW PAHs in mussels and oysters from 177 sites sampled nationwide during the 1986, 1987, and 1988 NS&T Mussel Watch surveys. The LMW PAH group included 10 two- and three-ring compounds such as naphthalene and anthracene as described in NOAA (1989). The HMW PAHs included 8 four- and five-ring compounds such as fluoranthene and B(a)p as described in NOAA (1989).

For LMW PAHs, the national median bivalve concentration was 180 ppb dw with a range of 2.7 to 4200 ppb dw (Table 14.9). By contrast, the regionwide median for mussels from 17 southern California sites was 22 ppb dw with a range of 2.7 to 1200 ppb dw. No other U. S. urban coastal area cited in Table 14.7 produced a lower median, and only the Chesapeake Bay mussels produced a comparable mean (203 in contrast to 204 ppb dw; Table 14.9). Some of the least contaminated mussels in the United States came from the Newport Bay West Jetty (2.7 ppb dw), the Oceanside Beach Jetty (3.0 ppb dw), and Palos Verdes (5.7 ppm dw).

For HMW PAHs, the median national U. S. bivalve concentration was 290 ppb dw and ranged from below detection limits to 11,000 ppb dw. By contrast, the regionwide median for mussels from 17 southern California sites was 8 ppb dw and ranged from below detection limits to 2700 ppb dw. No other U. S. urban coastal area cited in Table 14.10 had a lower median, and only the Chesapeake Bay and two Alaska sites had lower mean concentrations. The least contaminated mussels came from Imperial Beach, Point Loma, La Jolla, Newport Beach Jetty, Palos Verdes, and Santa Catalina Island (all contained levels of HMW PAHs below detection limits; NOAA 1989).

Any analyses of temporal trends in bivalves are severely limited since only B(a)p at a few sites can be compared. Any conclusions cannot be considered indicative of trends in PAHs in general. However, B(a)p levels in Los Angeles Harbor and Redondo Beach appear to be lower in the 1986 NS&T sampling than values reported by Gossett *et al.* (1982) for the early 1980s.

Preliminary results indicate that there were no significant changes in concentrations of LMW PAHs or HMW PAHs in mussels sampled for the NS&T Mussel Watch Program between 1986 and 1988 (NOAA, 1989). Concentrations of LMW PAHs declined slightly at Marina del Rey and Santa Cruz Island and increased at San Diego Bay. HMW PAHs declined slightly at Point Loma, Santa Catalina Island, and Santa Cruz Island and increased in Mission Bay.
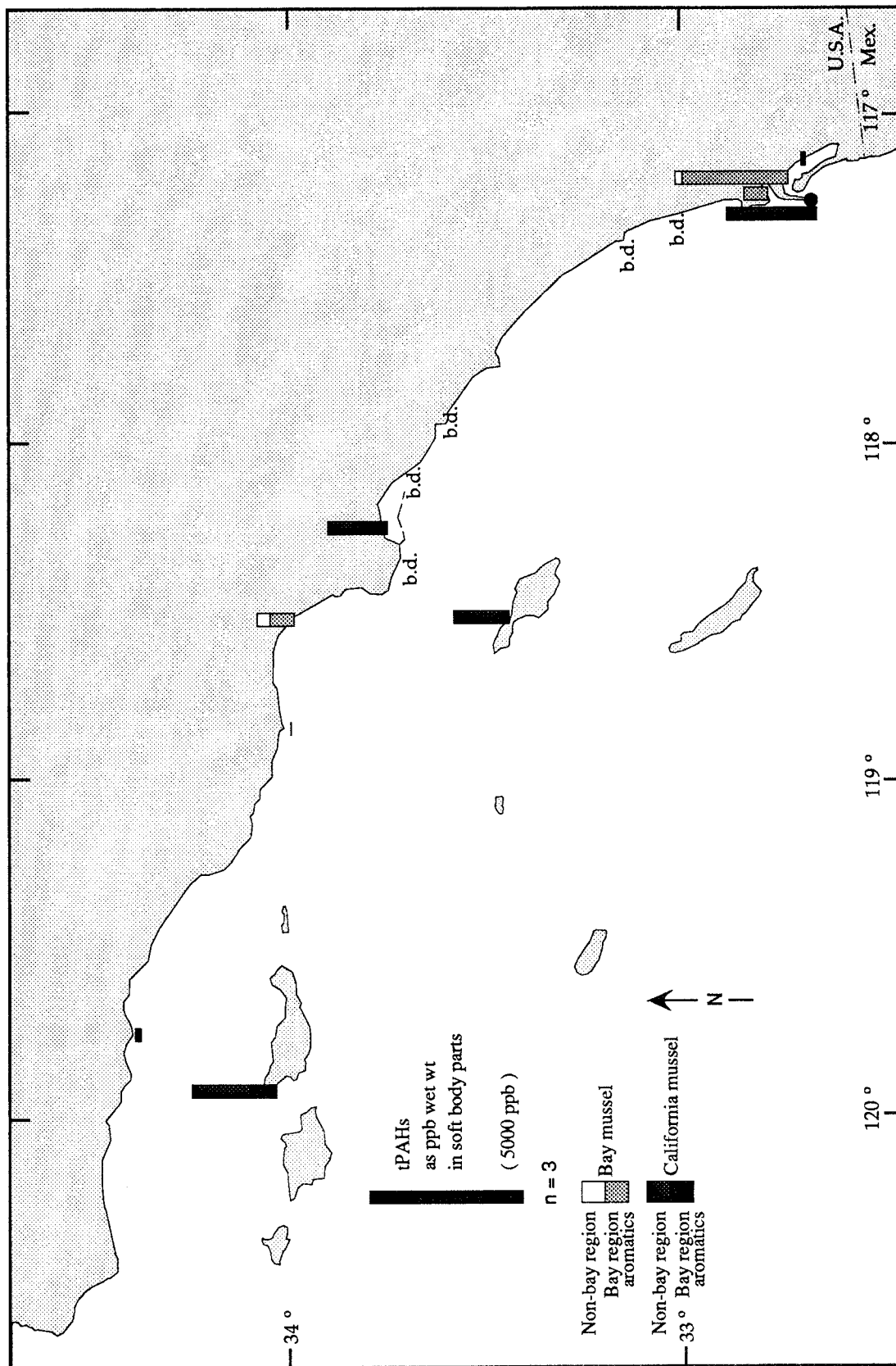
Figure 14.7. Total PAHs in mussels (NS&T Program). Source: NOAA, 1987.

Table 14.9. Comparison of concentrations (ppb dw) of LMW PAHs in bivalves (mussels and oysters) along the U. S. coast and in major coastal subregions. Based on data from three annual mussel watch surveys (1986, 1987, and 1988) as described in NOAA, 1989. N = number of sites.

Area	N	Median	Mean	SD	Minimum	Maximum
United States	177	180	364	602	2.7	4200
Atlantic Coast	59	390	483	525	8.8	2600
Mid-Atlantic Bight	35	355	454	505	8.8	2100
Long Island Sound	9	410	490	388	240	1500
New York Bight	7	660	866	852	8.8	2600
Chesapeake Bay	6	235	203	79	99	290
Gulf of Mexico	67	89	250	608	6.8	3700
Florida	18	105	522	1096	6.8	3700
Texas	27	61	130	170	11	680
Pacific Regions						
West Coast	46	64	381	695	2.7	4200
Southern California Bight	17	22	204	355	2.7	1200
Puget Sound	7	380	967	1440	180	4,00
Alaska	2	230	230	170	85	290
Hawaii	3	520	401	279	82	600

See Table 14.5 for list of compounds included in total.

Table 14.10. Comparison of concentrations (ppb dw) of HMW PAHs in bivalves (mussels and oysters) along the U. S. coast and in major coastal subregions. Based on data from three annual mussel watch surveys (1986, 1987, and 1988) as described in NOAA, 1989. N = number of sites.

Area	N	Median	Mean	SD	Minimum	Maximum
United States	177	290	648	1387	<1	11,000
Atlantic Coast	59	340	839	1593	9.6	11,000
Mid-Atlantic Bight	35	340	1024	1977	<1	11,000
Long Island Sound	9	900	991	964	230	3400
New York Bight	7	1450	2910	3702	260	11,000
Chesapeake Bay	6	170	226	88	130	370
Gulf of Mexico	67	120	381	586	7.2	2900
Florida	18	190	407	551	12	2000
Texas	27	59	438	735	7	2900
Pacific Regions						
West Coast	46	15	844	2043	0.5	11,000
Southern California Bight	17	8	340	787	<1	2700
Puget Sound	7	1200	2,01	3886	69	11,000
Alaska	2	12	12	15	1.6	23
Hawaii	3	1900	1337	1064	200	1064

See Table 14.5 for list of compounds included in total.

PAHs IN FISH AND OTHER SPECIES

Most marine organisms (other then bivalve mollusks) rapidly metabolize PAH compounds so that it is not possible to determine if they have accumulated PAHs based on analyses of parent compounds.

Some crustaceans do not rapidly metabolize PAHs. In 1951, Shimkin *et al.* (1951) isolated 2,3-benzopyrene from barnacles collected at the base of the south jetty at Newport Bay. In a follow-up report, Zechmeister and Koe (1952) further identified five other HMW PAHs: anthracene, phenanthrene, chrysene, fluoranthene, and 1,12-benzperylene. Concentrations were not reported, but the authors expressed concern that the frequently observed tarry substances seen along shore were contaminating marine life with mutagenic substances.

Aromatic hydrocarbons were not measured again in invertebrates or fish in the Southern California Bight for 25 years. Several hundred samples of fish, echinoderms, other invertebrates, and seaweeds were measured for aliphatic and aromatic hydrocarbons in surveys conducted as part of the 1976-78 Outer Continental Shelf (OCS) Program of the Minerals Management Service (MMS; formerly Bureau of Land Management). As stated in several reports (Rossi *et al.*, 1978a, 1978b, 1978c), there were no peaks of aromatic hydrocarbons that corresponded with PAH compounds. However, they did observe that the total aromatic fractions were higher in concentrations in deep macrobenthic organisms caught near the Los Angeles area compared to offshore sites.

Only one study, (Mearns and Young, 1980) conducted sampling for PAHs in invertebrate species besides mussels. They also analyzed PAHs in three fish species. Two additional studies using NS&T Program parameters to report levels of PAHs in fish were available to compare with NS&T data. Both these studies limited their sampling to the Los Angeles Harbor and Santa Monica Bay areas with Dana Point as a control. Gossett *et al.* (1982) examined B(a)p levels in the muscle of 15 different species among 13 sites. Malins *et al.* (1986a) analyzed the stomach contents of white croaker for PAHs, plus their bile for PAH metabolites.

Mearns and Young (1980) analyzed B(a)p in a spectrum of taxa ranging from primary producers (kelp) to tertiary carnivores (halibut). Samples were taken in 1979 from the San Pedro Bay area (Figure 14.8). Residues ranged over 2 orders of magnitude. B(a)p was highest in the northern anchovy (18.7 ppb) and lowest in muscles of white croaker and California halibut (1.7 ppb). Levels in the liver of the halibut were twice as high (3.4 ppb) as those in muscle tissue (1.5 ppb) or the GI tract (1.4 ppb). Kelp frond and gaper clam samples contained 5.4 and 8.8 ppb ww, respectively. Since different species have varying ability to metabolize B(a)p, exact interpretation of these data is difficult. However, they do indicate that B(a)p does not biomagnify.

Gossett et al. (1982) analyzed the muscle of various bottom fish collected at sites in Los Angeles Harbor and Santa Monica Bay in 1981. In all samples, B(a)p was not above the detection limit of 1 ppb ww. As a quality assurance check, archived tissues of white croaker from the sampling of Mearns and Young (1980) were also analyzed. Concentrations comparable to those reported by Mearns and Young were obtained (see Figure 14.8).

Malins et al. (1986a) sampled the stomach contents of white croaker collected from three sites in Los Angeles Harbor, near the Hyperion outfall in Santa Monica Bay, and off Dana Point in 1984 (Figure 14.9). Levels of PAHs reported by Malins et al. are much higher than those from NS&T (by roughly 1 order of magnitude). However, Malins' sampling sites were designed to be proximal to point sources; whereas, NS&T sites were chosen to be integrative of broader regions. Regardless of this difference, the regional patterns of PAHs in stomach contents are quite similar to those in sediments and mussels.

Since fish rapidly metabolize PAHs it is not surprising to find very low or undetectable concentrations in fish tissue from areas where sediments and food items are high in parent PAH compounds. The proof that fish from areas high in PAHs have been exposed to PAHs comes from measurements of PAH metabolites in bile fluid taken from the gall bladder and measured for fluorescent aromatic compounds (FAC) at wavelengths that can be used to quantify both LMW compounds and HMW compounds (Krahn et al., 1984). LMW compounds include 2-3 ring metabolites (naphthalene and others), while HMW compounds include 4-6 ring metabolites (pyrene, B(a)p, and others). Such measurements were made in bile samples of four species of fish (hornyhead turbot, white croaker, barred sandbass, and black croaker) collected at 14 NOAA NS&T Benthic Surveillance Program sites in 1984-87 (McCain et al., 1989; Varanasi et al., 1989) and, separately, in white croaker at 5 sites in December 1984 and 1 site (Cerritos Channel, inner Los Angeles Harbor) in August 1985 (Malins et al., 1987). Because these concentrations are calculated from fluorescence, they are relative rather than absolute concentrations.

As shown in Table 14.11, mean concentrations of LMW FAC in bile from all southern California fish sampled ranged nearly 100-fold from 9.6 ppm ww (μg per gram of bile) in hornyhead turbot from Dana Point to 900 ppm ww in barred sandbass from a site just south of the Coronado Bridge in San Diego Harbor (mean of 1984, 1985, and 1986 collections, Varanasi et al., 1989).

Due to possible interspecies differences in PAH metabolism and because no single species could be collected at all sites, each species-site collection must be compared to its own reference collection (such as Dana Point). In hornyhead turbot, collected only at coastal shelf stations (outside harbors and bays), mean concentrations of LMW FAC ranged 14-fold from 9.6 ppm ww at Dana Point (reference site) to 140 ppm ww at a site near the now-abandoned Hyperion sludge outfall ("Santa Monica Bay East" in Table 14.11). Mean concentrations were about 10 times reference at San Pedro Canyon (off San Pedro Bay) and at a site just outside and south of the entrance to San Diego Harbor (110 and 90 ppm ww, respectively). White croakers were collected at both harbor and coastal shelf sites. Mean concentrations of LMW FAC in white croaker ranged 50-fold from 17 ppm ww at Dana Point (reference site) to 410 ppm ww in fish from Reservation Point in Los Angeles Harbor (Table 14.11). By comparison, mean LMW FAC concentrations in white croaker from Los Angeles-Long Beach areas were about 3 to 4 times reference values. Barred sand bass were collected only from Dana Point and San Diego Harbor. Mean concentrations of LMW FAC in barred sandbass ranged 60-fold from 15 ppm ww at Dana Point (reference site) to 900 ppm ww at the South San Diego Bay site (Table 14.11). There is no reference data for interpreting the mean concentrations of 72 and 130 ppm ww in black croaker from 1987 San Diego Harbor collections (McCain et al., 1989; Table 14.11).
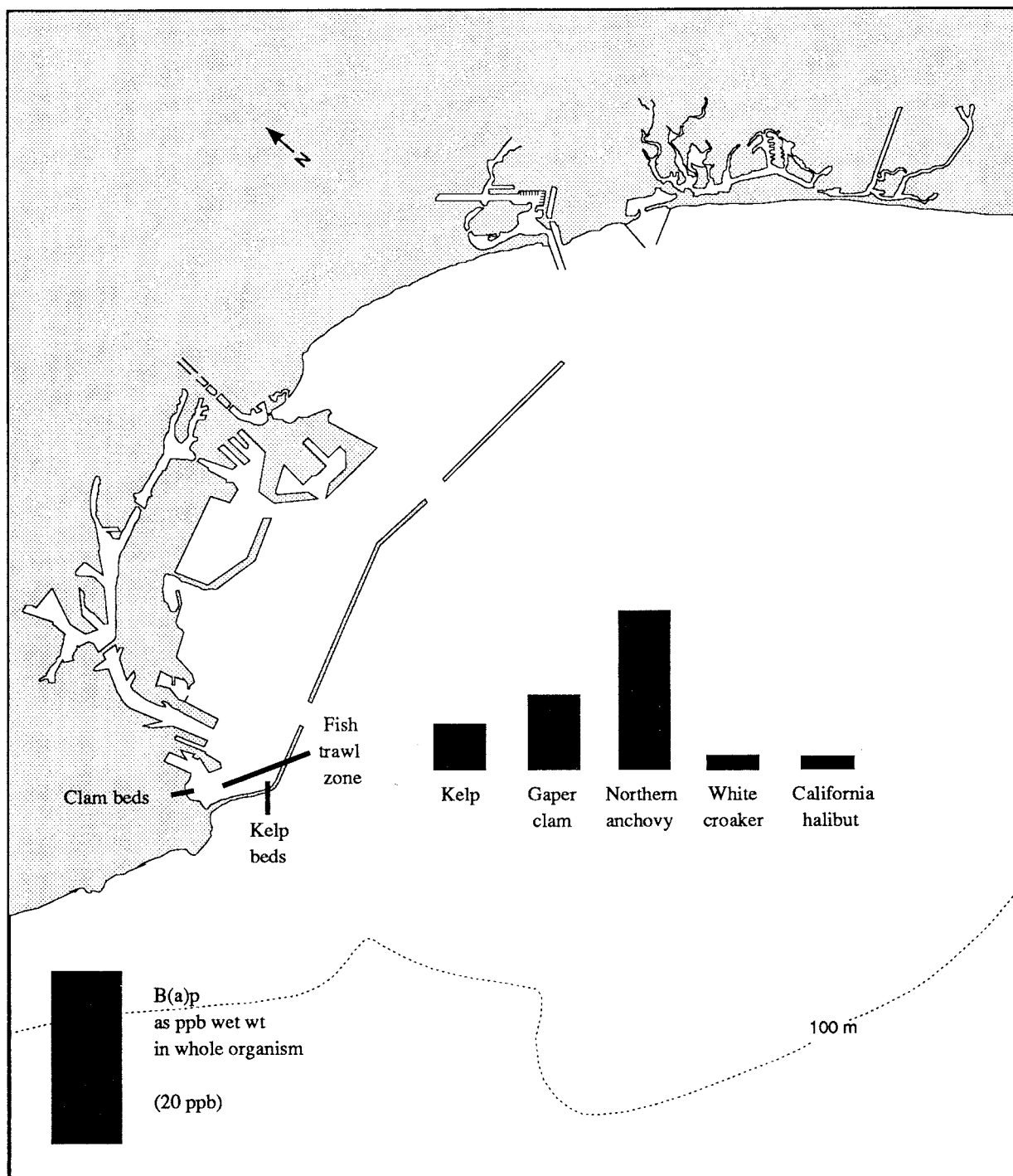
Figure 14.8. B(a)p in organisms of various trophic levels from Mearns and Young, 1980.
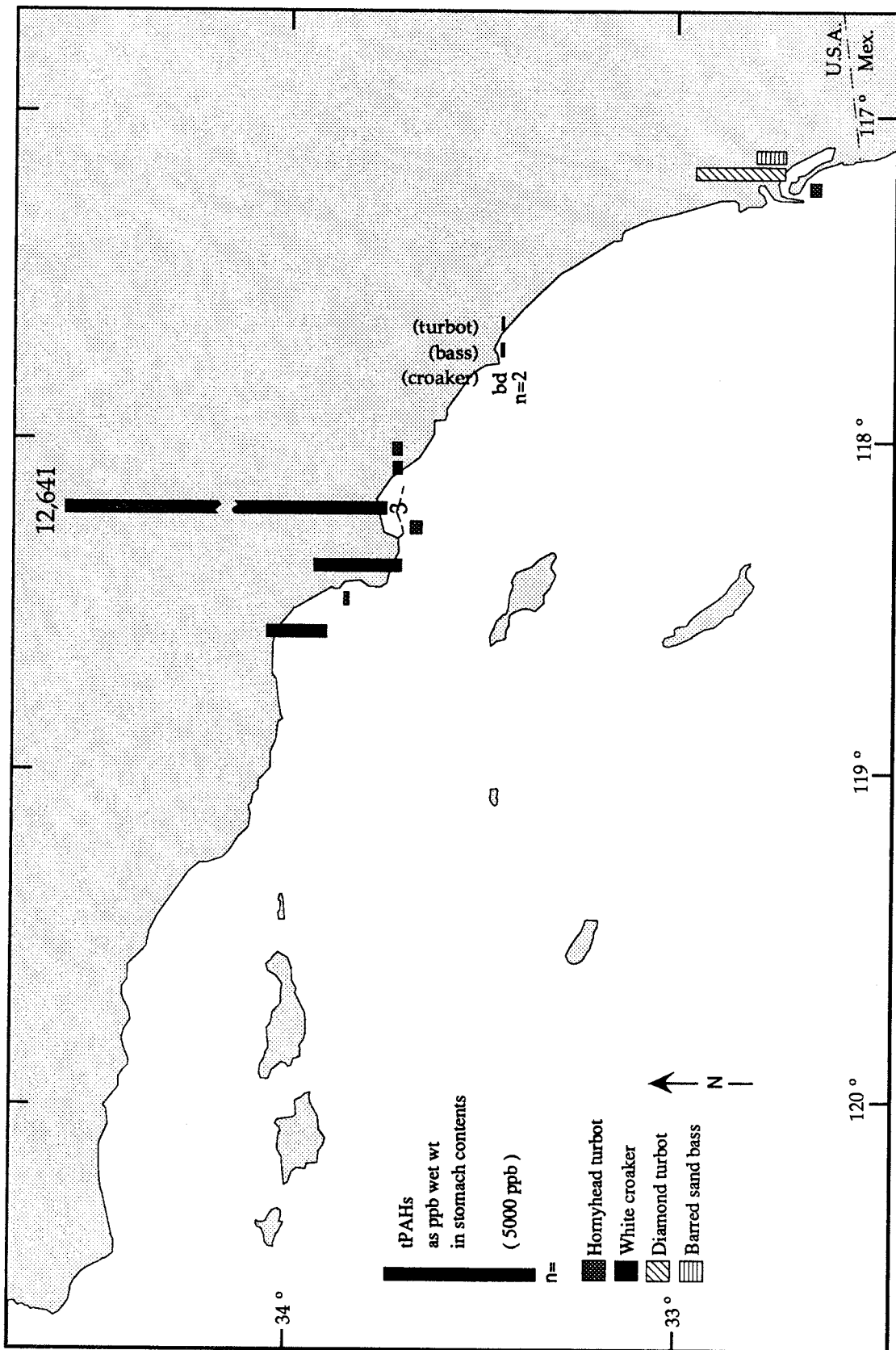
Figure 14.9. Total PAHs in fish stomach contents of bottom fish from Malins et al., 1986..

Similar intersite and interspecies differences also occurred for HMW FAC in fish bile. In hornyhead turbot, mean concentrations ranged 4-fold from 0.03 ppm ww at Dana Point (reference site) to 0.14 ppm ww in the fish from San Pedro Canyon (Table 14.12). Concentrations in hornyhead turbot from Santa Monica Bay and San Pedro Canyon sites (0.09 to 0.14 ppm ww) were intermediate but low (3 to 5 times reference). In white croaker, mean concentrations of HMW FAC ranged 100-fold from 0.05 ppm ww at Dana Point to 5.6 ppm ww at a site in Cerritos Channel (Los Angeles Harbor). In bile of barred sand bass (collected only at Dana Point, Mission Bay, and San Diego Harbor) mean HMW FAC concentrations ranged over 100-fold from 0.05 ppm ww in fish from Dana Point to 5.7 ppm ww in fish from the North San Diego Bay site (Table 14.12).

While Dana Point may be a suitable reference site for comparing with other areas, it may not be a completely PAH-free control site. At Bodega Bay in northern California, Varanasi *et al.* (1989) reported mean LMW and HMW FAC concentrations of 6.6 and 0.02 ppm ww, respectively in white croaker. These concentrations are about half the values for Dana Point (Tables 14.11 and 14.12).

While fish from San Diego Harbor and the Los Angeles-Long Beach areas generally had the highest concentration of FAC, it will be noted that those from several sites in Los Angeles Harbor and near Long Beach had higher (relative to reference) concentrations of LMW FAC than in San Diego Harbor. White croaker from San Diego Harbor had considerably higher relative concentrations of HMW FAC than fish from the Los Angeles area. Thus the two harbor areas differ in assemblages of PAHs accumulated by fish.

SUMMARY AND CONCLUSIONS

Marine life of the Southern California Bight has probably been exposed to low levels of PAHs for millenia as a result of inputs from natural oil seeps. However, significant inputs probably began 70 years ago with the onset of coastal oil drilling and attendant spillage and discharge of drilling wastes and refinery effluents into areas such as Los Angeles-Long Beach harbors and along the northern Orange County coast (Huntington Beach). Ocean dumping of drilling wastes during the 1950s and 1960s and refinery wastes during the 1960s, may have been the largest annual inputs; but, after this period, sewage and stormwater run-off dominated (about equally). Today, inputs of PAHs from sewage may be declining such that run-off may now be the dominant source. Despite occasional major spills of crude and fuel oil, these may be minor contributors to the Bight, though they were locally important where they occurred in remote areas such as off Point Conception or south of Ensenada.

PAHs in sediments along a portion of the mainland shelf in Los Angeles-Long Beach harbors and in San Diego Harbor have been documented at appropriate detection limits. Concentrations are surprisingly low in areas distant from the Los Angeles and San Diego Harbor areas and are among the most PAH-free sediment in the United States. However, there are clearly regions of exceptionally high PAH contamination centered in the Los Angeles-Long Beach harbors and San Diego Harbor near commercial, industrial, and military operations. Based on data from Orange County, PAH concentrations around sewage outfalls appear to be high only in the immediate vicinity of the diffuser. There is insufficient data to document long-term trends of PAH contamination in nearshore sediments. Cores offshore reveal little contamination in the San Nicolas Basin; but, in the San Pedro Basin there is a history of major aromatic hydrocarbon, and, presumably, PAH contamination during the 1950s and 1960s in concert with ocean dumping. Limited data from an Orange County site suggests there may be important seasonal variations of PAHs in sediments (high in winter, low in summer and fall).

Despite high concentrations of PAHs in sediments of the Los Angeles, Long Beach, and San Diego harbor areas and high inputs from sewage and run-off, mussels of the Southern California Bight contain the lowest PAH concentrations of any urban coastal area of the United States. The open coastal areas from Imperial Beach north to northern Orange County is nearly PAH free with respect to levels in mussels. However, concentrations are dramatically higher in harbor areas.

PAHs occur in tissues of seaweeds and some invertebrates, but are deceptively low in fish tissues. However, measurements of PAHs in stomach contents and PAH metabolites in bile indicate that fish from San Diego Harbor and several sites in the Los Angeles-Long Beach harbors area have been exposed to, taken up, and excreted high concentrations of PAH material.

Table 14.11. Summary of mean (± standard deviation) concentrations (ppm ww) of LMW FAC (fluorescent metabolites of 2-3 aromatic ring compounds) in bile of hornyhead turbot (HHT), white croaker (WC), black croaker (BC), and barred sandbass (BSB) from Bodega Bay and from 14 sites sampled in the NOAA Benthic Surveillance Program, 1984 through 1987.

Site	Year	N	HHT	WC	BC	BSB
Bodega Bay [1]	84,85,86	22	-----	6.6 ± 0.6	-----	-----
Bodega Bay [1]	87	---	-----	9 ± 0.7	-----	-----
Reference sites						
Dana Point [3]	84	8	-----	39 ± 13	-----	-----
Dana Point [1]	84,85,86		9.6 ± 13 (38)	21 ± 16 (25)	-----	15 ± 4.8 (14)
Dana Point [2]	87	----	10 ± 13	17 ± 14	-----	15 ± 5
Santa Monica Bay, West [1]	86	5	140 ± 59	-----	-----	-----
Hyperion [3] Santa Monica Bay	84	5	-----	64 ± 47	-----	-----
Santa Monica Bay, East [1]	84,85	27	60 ± 54	-----	-----	-----
Whites Point [3]	84	12	-----	170 ± 61	-----	-----
San Pedro Canyon [1]	84	14	110 ± 78	-----	-----	-----
Los Angeles/Long Beach Outer Harbor [1]	85,86	20	-----	53 ± 23	-----	-----
Cerritos Channel [3] Los Angeles Harbor	84	6	-----	330 ± 100	-----	-----
Reservation Point [3] Los Angeles Harbor	84	7	-----	410 ± 230	-----	-----
Long Beach [1]	85,86	28	-----	93 ± 54	-----	-----
Queensway Beach [3] Long Beach Harbor	85	11	-----	140 ± 52	-----	-----
Seal Beach [1]	84	14	-----	80 ± 34	-----	-----
Mission Bay [1]	86	2	-----	-----	-----	32 ± 3.5
Outside San Diego Bay [1]	84,85	-----	90 ± 74	-----	-----	-----
Outside San Diego Bay [2]	87	----	90 ± 74	-----	-----	-----
Shelter Island, San Diego Harbor [2]	87	-----	-----	-----	72 ± 34	-----
West Harbor Island [2]	87	-----	-----	61 ± 17	-----	-----
North San Diego Harbor [1]	86	-----	-----	130 ± 28	-----	-----
North San Diego Harbor [2]	87	-----	-----	130 ± 52	130 ± 23	400 ± 95
South San Diego Harbor [1]	84,85,86	-----	-----	-----	-----	900 ± 360
South San Diego Harbor [2]	87	-----	-----	-----	-----	650 ± 310
National City, San Diego Harbor [2]	87	-----	-----	-----	-----	400 ± 80

Sources: Varanasi et al., 1989
[2] McCain et al., 1989
[3] Malins et al., 1987

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Table 14.12. Summary of mean (± standard deviation) concentrations (ppm ww) of HMW FAC (fluorescent metabolites of 4-6 aromatic ring compounds) in bile of hornyhead turbot (HHT), white croaker (WC), black croaker (BC), and barred sandbass (BSB) from Bodega Bay and from 14 sites sampled in the NOAA Benthic Surveillance Program, 1984 therough 1987.

Site	Year	N	HHT	WC	BC	BSB
Bodega Bay [1]	84,85,86	22	-----	0.02 ± 0.016	-----	-----
Bodega Bay [1]	87	—	-----	≤0.1	-----	-----
Reference sites						
Dana Point [3]	84	8	-----	0.08 ± 0.08	-----	-----
Dana Point [1]	84,85,86		0.03± 0.05 (38)	0.05 ± 0.06 (25)	----- -----	0.05 ± 0.06 (14)
Dana Point [2]	87	----	≤0.1	≤0.1	-----	≤0.1
Santa Monica Bay, West [1]	86	5	0.12 ± 0.10	-----	-----	-----
Hyperion [3] Santa Monica Bay	84	5	-----	0.08 ± 0.03	-----	-----
Santa Monica Bay, East [1]	84,85	27	0.09± 0.10	-----	-----	-----
Whites Point [3]	84	12	-----	0.96 ± 1.6	-----	-----
San Pedro Canyon [1]	84	14	0.14 ± 0.11	-----	-----	-----
Los Angeles/Long Beach Outer Harbor [1]	85,86	20	-----	0.140 ± 0.10	-----	-----
Cerritos Channel [3] Los Angeles Harbor	84	8	-----	5.55 ± 1.20	-----	-----
Reservation Point [3] Los Angeles Harbor	84	7	-----	3.70 ± 3.10	-----	-----
Long Beach [1]	85,86	28	-----	0.11 ± 0.11	-----	-----
Queensway Beach [3] Long Beach Harbor	85	11	-----	0.33 ± 0.16	-----	-----
Seal Beach [1]	84	14	-----	0.22 ± 0.27	-----	-----
Mission Bay [1]	86	2	-----	-----	-----	1.2 ± 0.2
Outside San Diego Bay [1]	84,85	18	.082 ± 0.07	-----	-----	-----
Outside San Diego Bay [2]	87	----	≤0.1	-----	-----	-----
Shelter Island, San Diego Harbor [2]	87	----	-----	-----	2.5 ± 3.7	-----
West Harbor Island [2]	87	-----	-----	2.3 ± 2.7	-----	-----
North San Diego Harbor [1]	86	12	-----	1.4 ± 1.1	-----	-----
North San Diego Harbor [2]	87	-----	-----	1.8 ± 1.4	2.1 ± 2.5	1.4 ± 0.9
South San Diego Harbor [1]	84,85,86	-----	-----	-----	-----	5.7 ± 4.5
South San Diego Harbor [2]	87	-----	-----	-----	-----	3.7 ± 2.9
National City, San Diego Harbor [2]	87	-----	-----	-----	-----	2.8 ± 0.60

Sources: [1] Varanasi *et al.*, 1989
[2] McCain *et al.*, 1989
[3] Malins *et al.*, 1987

Although direct correlations have not been attempted for this report, apparently there has been good agreement among various surveys about the regional patterns of PAH contamination in sediments, mussels, fish stomach content, and bile metabolites. The major harbors (Los Angeles-Long Beach and San Diego) are clearly epicenters of contamination at all ecosystem levels. There may, however, be important local differences in the kinds and patterns of contamination. Lower molecular weight (for example, napthalene) PAHs are more important in the Los Angeles area; whereas HMW compounds (such as B(a)p) may be more important in San Diego Harbor.

INFORMATION NEEDS

Historical and current inputs of PAHs to the Southern California Bight can only be estimated from a few measurements and with many assumptions. Estimates of inputs, such as those provided in this chapter, need to be confirmed by actual measurement of PAHs at appropriate detection limits in specific waste media (crude oil, fuel oils, sewage, run-off water, oil seepage) to provide a solid basis for management alternatives.

Use of low detection limits (1 ppb per analyte) would be useful in confirming the apparently low concentrations in sediments of PAHs on the Santa Barbara mainland shelf and elsewhere in the Santa Barbara Basin. This area has been subject to offshore drilling for over 30 years. It suffers from chronic seepage and has experienced the region's largest oil spill. Yet, today, it appears to be virtually free of PAHs except around the wreck of the Pacific Baroness in deep water off Point Conception. This contrasts sharply with the high levels of PAH found in sediments and marine life around a Gulf of Mexico seep (Wade et al., 1989). Despite numerous measurements during the mid- and late-1980s, survey grids have not been of sufficient detail to determine the scale of PAH "hot spots" in the Los-Angeles-Long Beach area and in the San Diego Harbor area. For example, it is not clear if the high level of PAHs measured at six or seven sites near industrial or military areas are representative of conditions throughout San Diego Bay. Large areas of the southern and western portions of the bay should be surveyed. The sediment of Santa Monica Bay has been inadequately surveyed to determine PAH distribution. Likewise, the PAH burden of sediments of the San Pedro Basin is not known, but could be large as a result of ocean dumping of oil-related wastes in the 1950s and 1960s. Use of low detection limits may also be required to address adequately the PAH burden of sediments around sewage outfalls and confirm a possible seasonal variation of PAH concentrations.

Continued monitoring of PAHs in mussels from near urban areas, and at Santa Cruz and Santa Catalina islands, is needed to determine long-term trends. Although largely PAH-free, mussels from selected non-urban areas should be monitored as well to confirm that concentrations do not rise. The source or sources of PAHs in mussels from Santa Cruz Island (Frazer Point) and Santa Catalina Island (Bird Rock) need to be determined. These areas may be near active seeps.

It is not necessary or practical to monitor PAHs in fish tissues. However, measurements of PAH metabolites (in the form of FAC) in fish bile are an important tool that should be used elsewhere in the Bight including the Santa Monica Bay, along the Santa Barbara shelf, in bottom fish from the San Pedro Basin, and in fish from Santa Cruz and Santa Catalina islands.

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CHAPTER 15

POLYCHLORINATED BIPHENYLS

As a class of organic compounds, polychlorinated biphenyls (PCBs) include 209 synthetically halogenated aromatic hydrocarbons. They were first prepared in 1881, but were not used commercially until around 1930 (Eisler, 1986c). PCBs were manufactured in the United States from 1929 to 1977. The Monsanto Industrial Chemicals Company was the major producer of PCBs in the United States and marketed them under the trade name Aroclor. A four-digit designation denoted individual formulations (for example, Aroclor 1242, Aroclor 1254), with the last two numbers representing the average percent chlorine composition by weight. Aroclor mixtures were produced by chlorination of biphenyl with chlorine gas to reach desired physical and chemical properties, but their composition has varied from batch to batch (Erickson, 1986). PCBs in the environment have been measured and reported in terms of commercial mixtures (Aroclors), by chlorination number, and by individual PCB compounds (congeners).

Their high stability and low flammability have enabled PCBs to be employed in a wide variety of industrial applications. Some of these uses include: insulating materials in electrical capacitors and transformers; hydraulic fluids; plasticizers in waxes; additives in paints, adhesives, and caulking compounds; and components in the manufacture of paper (U.S. EPA, 1984).

PCBs are among the most stable chemicals known, and rates of chemical degradation in the environment are thought to be slow. While this stability is one reason PCBs have proven to be useful in industrial applications, the prominence of the compounds as contaminants stems in part from this presumed persistence. Concern about environmental contamination by PCBs has been a more recent phenomenon than that for DDT. As has been the case for many chemical compounds, large-scale tragedies provided the impetus for research into environmental effects and regulation of manufacture and use. In 1968, rice oil contaminated with PCBs, was used by about 1300 people in Yusho, Japan. The contaminated oil caused skin lesions, eye discharges, abdominal pain and reproductive and nervous system disorders. There also has been some indication of increased incidences of cancer among those exposed (U.S. EPA, 1984). In the natural environment, bioaccumulation of PCBs in waterfowl was identified as the cause of death for thousands of birds in the Irish Sea in 1969 (Levi, 1987).

Despite these instances of PCB poisoning, the acute toxicity of PCBs is relatively low compared to other chlorinated hydrocarbons. DDT for example, is approximately 100 times more acutely toxic than are PCBs (Clesceri, 1980). However, because of widespread dispersal of the compounds throughout the environment and their resistance to degradation, chronic toxicity of PCBs represents a serious environmental concern. Chronic exposure in birds has been shown to result in a number of systemic complications and reproductive impacts. According to Clesceri, the effects of PCB exposure on aquatic organisms are more subtle because of limited water solubility of the compounds, but it is pointed out that complex food web dynamics complicate delineation of impacts.

Several of the 209 possible PCB compounds have mutagenic and carcinogenic toxic properties similar to dioxin, and some of these have been found in marine samples at concentrations far exceeding toxic levels of associated dioxins (Kannan et al., 1989). These congeners occur in commercial Aroclor preparations (such as Aroclors 1242, 1248, 1254, and 1260, Kannan et al., 1988). In a recent assessment of cancer risk to average consumers of fish from U.S. estuarine and coastal waters, Connor (1989) estimated that 70 percent of the risk is associated with PCB contamination. However, Gossett et al. (1989) did not find increased levels of PCBs in blood of people consuming fish from the Los Angeles coastal area.

Laboratory studies have indicated that organic contaminants (especially PAHs) can be oxygenated to metabolite compounds in sediments, invertebrates, and fish. Brown et al. (1987) measured parent PCB compounds and oxygenated metabolites in *M. californianus* and reported that oxygenated metabolites of PCBs comprised 90 to 98 percent of all PCB compounds measured. However, Gossett (1988) reported that these results were not reproducible using different GC/MS instruments. The results of Brown et al. (1987) may therefore be questionable.

Because PCBs have been so widely used in a diversity of applications, sources of PCBs to the environment are varied. Point sources can be significant. For example, a capacitor manufacturing plant on the Hudson River discharged large amounts of waste laden with PCBs for a number of years, resulting in heavy contamination of sediments and striped bass (as summarized in Mearns et al., 1988). In many

regions, discharges from municipal waste treatment plants may represent relatively large point source inputs of PCBs. However, PCBs may also enter the environment from nonpoint sources, such as industrial runoff, leaching from disposal sites, and refuse incineration. Recent investigations by Yasuhara and Morita (1988) have indicated that thermal decomposition of such commonly used materials as plastic wrap (poly vinylidene chloride) may result in the formation of toxic chlorinated compounds, including PCBs, at temperatures as low as 200°C. This suggests that landfills and other disposal sites could represent diffuse but potentially large reservoirs for PCB input even in the absence of parent PCB compounds at the sites.

Upon introduction into the environment, transport mechanisms include both waterborne means and atmospheric deposition (Clesceri, 1980), although the latter has been identified as the more significant on a global scale. Atlas et al. (1986) estimated that as much as 98 percent of PCB input to the oceans comes from aerial deposition.

For the year 1971, SCCWRP (1973) estimated that of 44 mt of PCBs entering the Bight from non-advective sources, 57 percent (28 mt) was from ocean dumping, 23 percent (10 mt) from wastewater discharges, 9 percent (4 mt) from vessel coating, 4.5 percent (2 mt) from direct rainfall, and 0.5 percent from surface run-off. As a result of source control, inputs from municipal waste discharges decreased dramatically over the past 15 years from about 10,000 kg per year in 1972 to 820 kg in 1985 (Figure 15.1) and to 250 kg in 1987 (SCCWRP, 1987a). Mass emissions can no longer be computed since concentrations in sewage are now generally below detection (SCCWRP, 1989). By comparison, total PCB (tPCB) inputs by way of run-off through the Los Angeles River were 180 kg in 1971 and 1972, 210 kg in 1979 and 1980, and 9 kg in 1985 and 1986. However, for one storm in 1986 (September 22-25), tPCB emissions were 4.6 kg or 10 times the 3-day emission from the Hyperion outfall in Santa Monica Bay (0.45 kg). The three largest emissions came from the Los Angeles River (3.2 kg), Ballona Creek into Marina del Rey (1.2 kg), and the San Gabriel River (0.2 kg; SCCWRP, 1986). Thus, at least during wet periods, inputs from run-off may exceed those from sewage.
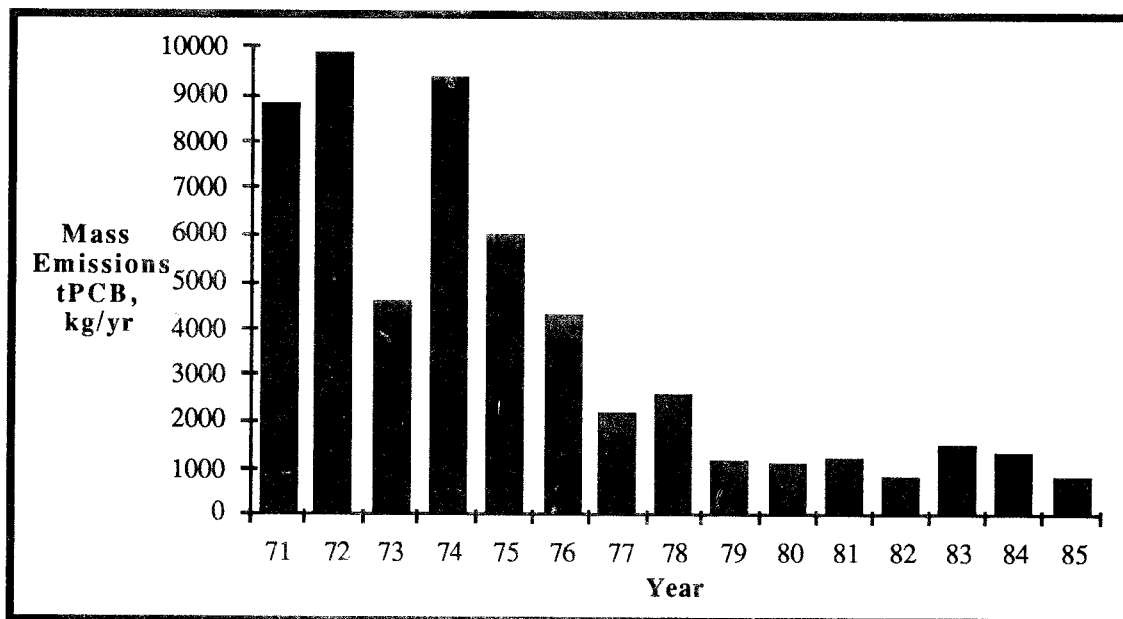

Figure 15.1 Combined annual mass emissions of tPCB for seven southern California municipal wastewater dischargers, 1971 to 1985. Source: SCCWRP, 1987a.

These figures belie the possibility that direct, dry weather fallout may have been an important input route for PCBs to the Bight because of onshore production of PCB aerosols. The source-strength of PCB inputs to the atmosphere in 1972 from Los Angeles was estimated to range from 20 to 35 mt per year (McClure, 1976; Rothschild, 1974); San Diego was estimated to emit 7 mt into the atmosphere

(Rothschild, 1974). About 6 mt per year (30% of the total estimate) was estimated to fall directly into coastal waters within 100 km of the urban areas (McClure, 1976). For 1973-74, Young and Heesen (1975) measured a direct dry-weather input of 1.8 mt into the 20,000 square km area adjacent to the coastline. They concluded that since 1974, and possibly earlier, dry aerial fallout has been the dominant route by which Aroclor 1254 is transferred from southern California to the coastal ecosystem (Young, Heesen, and McDermott, 1980a and b). Thus, during the early 1970s, aerial fallout was second only to municipal wastewaters as a source of PCB to the Bight. Aerial inputs have not been measured since then. With the major reduction of wastewater inputs to 0.25 mt per year (competitive with run-off), it is possible aerial fallout may now be the dominant regional route of entry of PCBs to the Bight. Estimates of total inputs have been adjusted periodically and new measurements by SCCWRP are currently underway.

Although direct assessments of PCB levels in the marine environment are not available prior to 1970, indirect observations permit inference of earlier temporal trends. For example, Hom et al. (1974) analyzed dated oceanic sediments from the Santa Barbara Basin of the Southern California Bight to elicit trends beginning as early as 1890 and found that deposition of PCBs began in about 1945. Concentrations rose steadily through 1967, the final year of dating for the analysis.

Summers et al. (1988) summarized records of the U.S. Tariff Commission and provided a breakdown of U.S. PCB usage by type of application, from 1929 to 1986. If the assumption is made that inputs to the marine environment have reflected patterns of general use, then peak inputs to the Bight occurred between 1965 and 1970 (Figure 15.2). PCBs have not been used in manufacturing in the United States since 1979 (Figure 15.2). However, monitoring of wastewater and sediment confirms that some input is continuing, but at levels perhaps 1 percent of those of the early 1970s. There remains, however, the major uncertainty of atmospheric inputs.
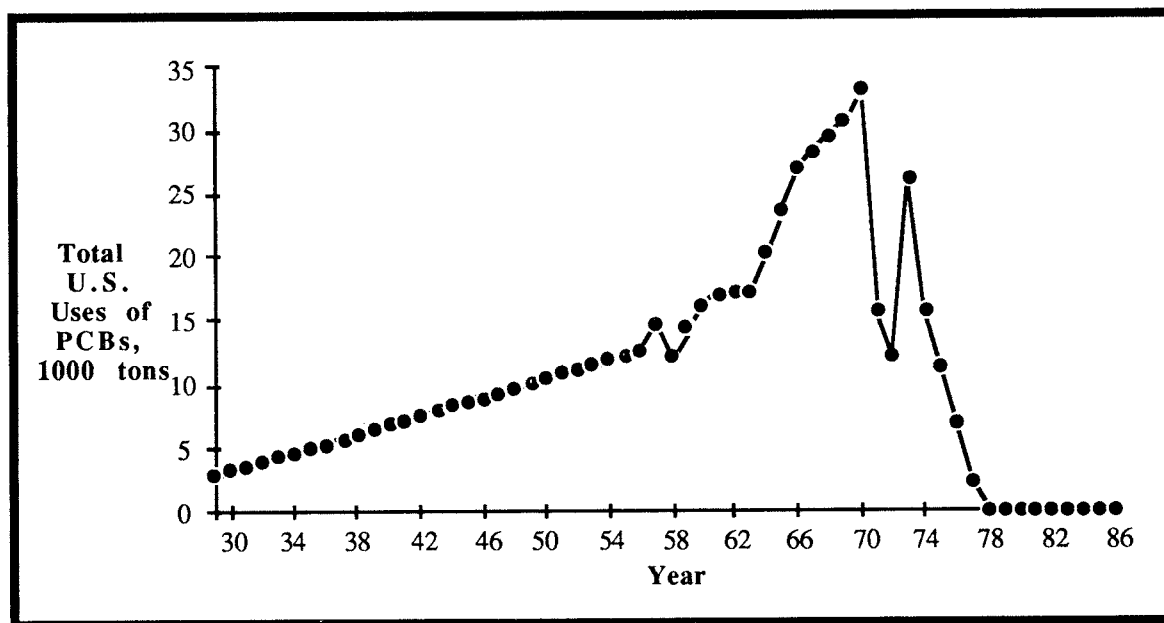

Figure 15.2. Mass of PCBs used in various United States applications, 1929 through 1986. Extracted from reports of U.S. Tariff Commission. Source: Summers et al., 1988.

The methods of measuring and reporting PCBs have changed considerably during the past 20 years, making it difficult to compare data sets. PCBs were not widely known to be contaminants of the Southern California Bight until 1969 (based on fish collected in 1965; Risebrough, 1969). During the 1970s and most of the 1980s, PCBs in environmental samples were reported in terms of commercial preparations (for example, Aroclor 1242 and Aroclor 1254) and were analyzed and monitored mainly by local and state agencies (municipalities, SCCWRP, and the California Department of Fish and Game). At first, (1971-73)

only concentrations of Aroclor 1254 were reported. Thereafter, these agencies reported concentrations of other commercial mixes including Aroclors 1242, 1248, and 1260. NOAA researchers initially reported PCBs in fish in terms of the commercial mixes (Stout and Beezhold, 1981; Gadbois and Maney, 1983).

However, from 1984 to 1987, NOAA's NS&T Program measured and reported PCBs in sediments, mussels, and fish in terms of chlorination number (2 through 10). In 1988, the NS&T Program converted to reporting PCBs in terms of 18 of the 209 congeners, but also analyzed some samples using both techniques and provided conversion factors so that the sum of PCBs (tPCB) reported by those congeners could be related to the sum of PCBs reported by chlorination number (NOAA, 1989). To convert from the sum of chlorination levels to the sum of 18 congeners, values should be divided by approximately 2. Also in 1988-89 surveys, the CMW began reporting PCBs in terms of 19 congeners (17 of which were in common with the NS&T Program). In addition, the CMW also measured and reported PCBs by commercial mix (in this case, Aroclors 1248, 1254, and 1260). When available, these data should provide a means of comparing tPCBs between the two reporting methods.

Eganhouse and Gossett (in press) estimate that the error associated with analysis of commercial PCB mixtures can be as high as 200 percent and can vary in either direction. This is because environmental samples do not usually closely match Aroclors in composition of PCB compounds, as well as that the same congeners are present in several mixtures. Although error associated with analyses of PCBs measured as individual congeners is lower than that for commercial mixtures, some error still exists because chromatographic columns cannot separate all 209 congeners (Eganhouse and Gossett, in press).

PCBs IN SEDIMENT

PCBs have been among the most commonly measured contaminants in sediments of the bays, harbors, shelf, slope, and offshore areas of the Bight. Concentrations reported from 12 extensive surveys span 6 orders of magnitude, from the minimum of 0.0002 ppm dw measured off Point Loma in 1985, to 34.2 ppm dw found in San Diego Harbor in 1983 and 55 ppm dw at a site at Palos Verdes in 1985 (Table 15.1). Results in Table 15.1 are grouped by general site type: rural coastal shelf, outfall areas, and bays and harbors. Although relatively low sediment PCB concentrations (less than 0.02 ppm dw) were found in all groups, high concentrations (more than 2 ppm dw) occurred in harbors and at one outfall site. As might be expected, the rural coastal shelf region had low concentrations and a limited range of values (0.005 to 0.039 ppm dw). While reporting and methodological differences among surveys do not permit extensive interpretation or comparison of these results, it can be noted that regions with highest reported mean values of sediment PCB included San Diego Harbor (2.25 ppm dw), the Palos Verdes shelf (0.676 ppm dw), and Los Angeles-Long Beach harbors (2.63 ppm dw). It is important to note that there is a lack of data from several harbors and bays. For example, PCBs were not measured in surveys of Lower Newport Bay (Liu and Schneider, 1988) or in the Tijuana estuary.

Results from large-scale synoptic sediment studies conducted by SCCWRP in 1977 and 1985 along the 60-m isobath are shown in Figures 15.3 and 15.4. During both surveys, the highest concentrations in coastal sediments occurred along the Palos Verdes shelf, but, in 1977 (Figure 15.3) there were also peaks adjacent to outfalls in Santa Monica Bay and off Orange County and Point Loma.

PCBs were measured by NOAA's NS&T Program Benthic Surveillance Project in 1984 and 1985 and by the Mussel Watch Project in 1986. Within these data sets, the three regions noted above--Palos Verdes, Los Angeles-Long Beach harbors, and San Diego Harbor--are consistent in their prominence as areas in which relatively elevated sediment concentrations of tPCBs (summed chlorination levels) were found. In 1984 and 1985, the Benthic Surveillance Project collected and analyzed sediments from six southern California sites. In both years, the site in San Diego Harbor had the highest PCB concentrations, 0.42 ± 0.13 ppm dw in 1984 and 0.64 ± 0.34 ppm dw in 1985. The San Pedro Canyon site yielded sediments with 0.16 ± 0.06 ppm dw in 1984, and 0.20 ± 0.06 ppm dw in 1985. The 1984 mean for the Seal Beach site was 0.05 ± 0.02 ppm dw, while the 1985 Long Beach mean was 0.21 ± 0.05 ppm dw. In contrast, the mean for 2 years of sampling at the other three sites (Outer San Diego Bay, Dana Point, and Santa Monica Bay) was 0.01 ± 0.007 ppm dw.

Table 15.1. Mean, median, minimum, and maximum tPCB concentrations in surface sediment from selected surveys, 1973 through 1988 in ppm dw.

Site	Year	N	Mean	Median	Minimum	Maximum	SD	Source
Islands								
Anacapa [c]	1985	1	0.00053					10
Santa Barbara[c]	1985	5	0.00037		0.00028	0.00050		10
North Santa Catalina[c]	1985	6	0.00054		0.00034	0.00087		10
South Santa Catalina[c]	1985	2	0.00095		0.00077	0.00120		10
San Pedro Basin								
North control[c]	1985	2	0.0020		0.0009	0.0046		10
Dumpsite 1[c]	1985	3	0.0038		0.0013	0.0120		10
Dumpsite 2[c]	1985	3	0.0061		0.0017	0.0220		10
South Control[c]	1985	2	0.0028		0.0012	0.0069		10
Rural Coastal Shelf (60 m only):								
Santa Barbara shelf	1977	6	0.013	0.01	0.005	0.031	0.01	1
	1985	4	0.013	0.014	0.005	0.019	0.006	2
Port Hueneme to Point Dume	1977	2	0.013		0.009	0.016	0.005	1
	1985	2	0.026		0.012	0.039	0.019	2
Newport to Dana Point	1977	2	0.014		0.007	0.02	0.009	1
	1985	1	0.014					2
Point Dume[c]	1985	2	0.013		0.013	0.014		10
Outfall Areas:								
Santa Monica Bay	1977[b]	10	0.157	0.094	0.031	0.513	0.153	1
	1985	3	0.092	0.106	0.057	0.114	0.031	3
5-Mile outfall [c]	1985	2	0.130		0.102	0.173		10
Palos Verdes shelf	1977[b]	8	2.76	2.00	0.109	10.9	3.56	1
	1985	11	0.676	0.572	0.048	1.83	0.602	3
Whites Point outfall [c]	1985	2	1.5		0.040	55.0		10
Orange County shelf	1977[b]	5	0.077	0.032	0.014	0.254	0.101	1
	1985	9	0.024	0.015	0.015	0.093	0.026	4
Point Loma Shelf	1985	8	0.0002	0.0002	0.0002	0.0002	0	5
Bays and Harbors:								
Los Angeles-Long Beach harbors [a]	1973	31	0.90	0.69	0.063	3.20	0.66	6
	1978	31	0.172	0.067	0.015	1.25	0.25	7
	1988	20	2.63	0.54	0.049	30.1	6.92	11
Marina del Rey [a]	1988	13	ND (<.001)	ND	ND			12
Upper Newport Bay [a]	1980	8	0.02	0.01	ND	0.05	0.01	8
San Diego Harbor [a]	1983	20	2.25	0.427	0.2	34.2	7.55	9
OVERALL		**224**			**0.0002**	**55.0**		

a - all depths; b - 60-m only; c - geometric means

1 Word and Mearns, 1979
2 Thompson et al., 1987
3 Hyperion Treatment Plant, original data
4 CSDOC, original data
5 City of San Diego, original data
6 Chen and Lu, 1974

7 Soule and Oguri, 1980a
8 MBC and SCCWRP, 1980
9 Ladd et al., 1984
10 Risebrough, 1987
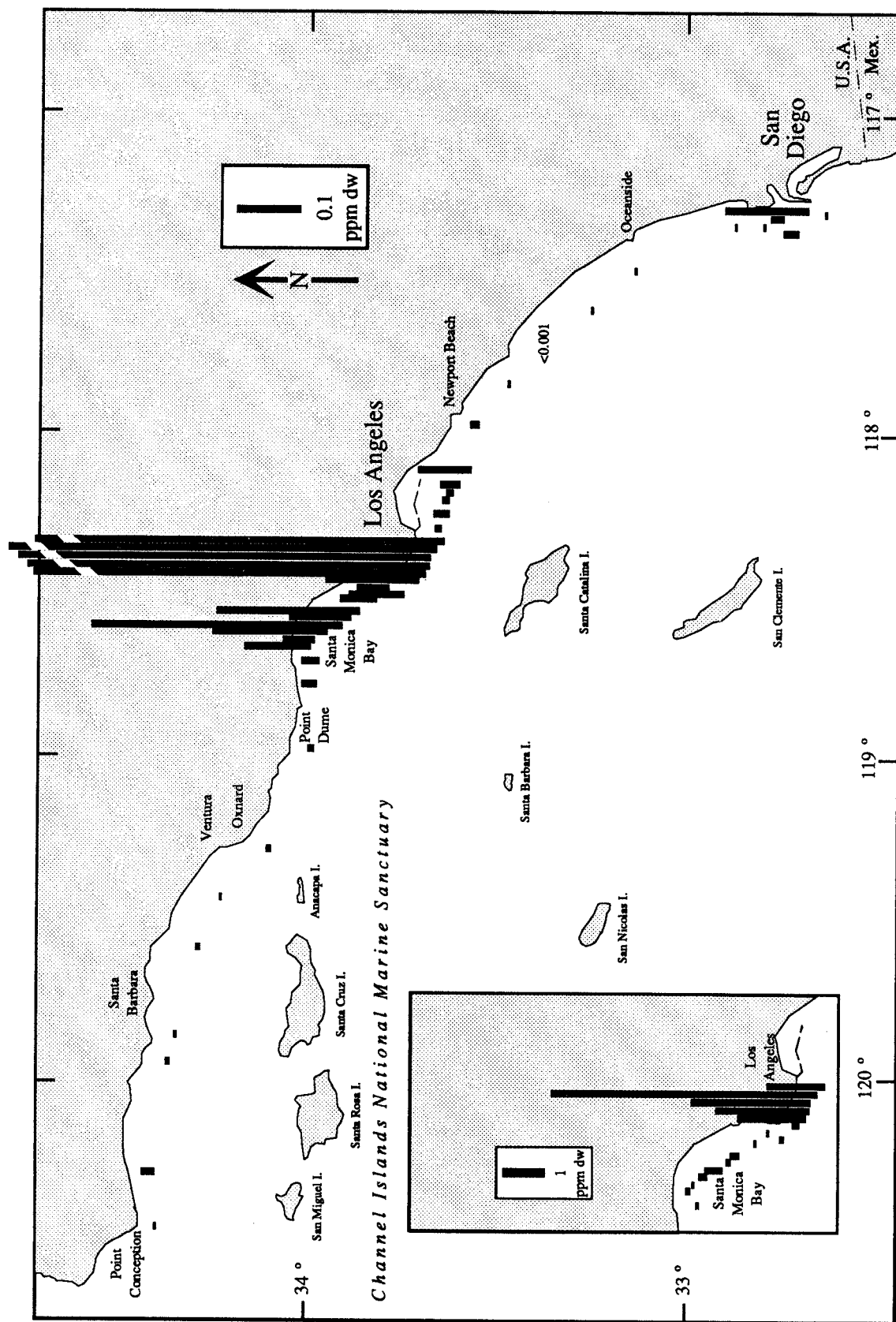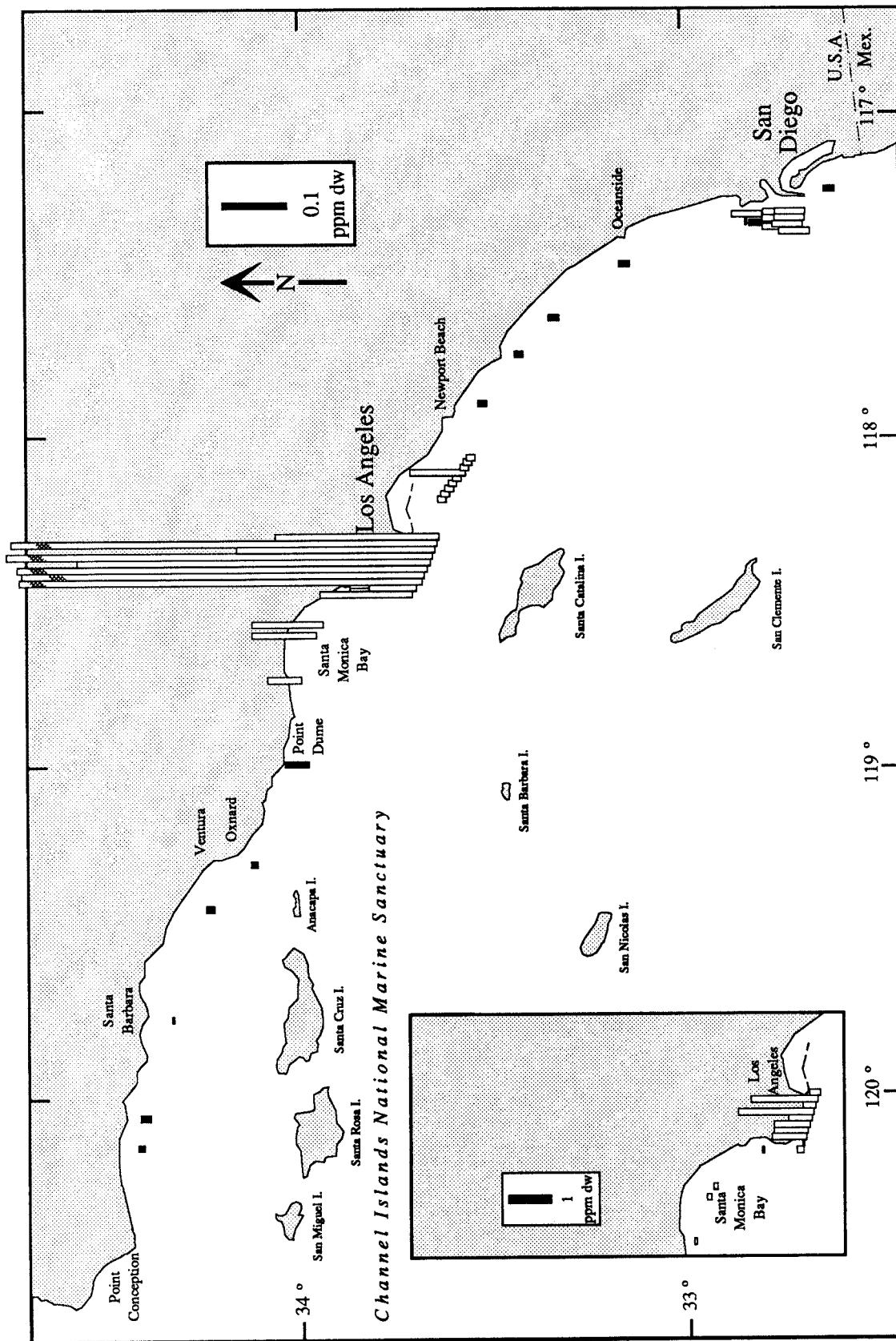11 Eganhouse et al., 1990
12 Soule and Oguri, 1990

Figure 15.3. Aroclor 1254 concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line, based on data from the 60-Meter Control Survey performed from April through August 1977 (Word and Mearns, 1979). Those sites with 1254 concentrations either too low or too high to fit the scale of the columns are indicated by the concentration value in ppm dw (low values) or a broken column with the value (high values). Inset bar scale is 1/15 that of main map.

Figure 15.4. Aroclor 1254 concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line for 1985; the black bars are from Thompson, et al., 1987, while the white bars are from data obtained from various sanitation districts (City of Los Angeles, Los Angeles, Orange, and San Diego counties). The scale of the bars in the inset is 1/15 that of the main map bars.

A somewhat different ranking results from the 10 southern California sites sampled in 1986 for the NS&T Mussel Watch Project. The three highest mean sediment concentrations were measured at Palos Verdes/Royal Palms (0.53 ± 0.26 ppm dw), Los Angeles-Long Beach fishing pier (0.23 ± 0.08 ppm) and San Diego/Harbor Island (0.15 ± 0.11 ppm dw). As a basis for comparison, the mean concentration measured at the other seven southern California sites was 0.03 ± 0.02 ppm dw. Nearly the same pattern was evident from 1987 sediment results. Of 11 locations sampled in the Southern California Bight, the Palos Verdes/Royal Palms site yielded the highest mean PCB concentration, at 0.60 ± 0.29 ppm; followed by the Los Angeles-Long Beach fishing pier site, 0.16 ± 0.04 ppm dw; and San Diego/Harbor Island, 0.06 ± 0.04 ppm dw. The mean for the other eight sites was 0.03 ± 0.02 ppm dw.

How does PCB contamination in sediments of the Southern California Bight compare on a national scale? Based on 1984-87 NOAA NS&T data that has been *normalized* to *fine-grained fractions* of sediment (NOAA, 1988), the mean and median tPCB concentrations in sediments at 18 southern California sites were 0.235 and 0.088 ppm dw, respectively (range, 0.017 to 0.977) or nearly double the national mean and median (0.147 and 0.036 ppm dw; 172 sites; Table 15.2). The Southern California Bight ranked second in terms of mean and median sediment PCB concentrations among four major urban coastal zones of comparable size and sampling effort: 1) Mid-Atlantic Bight, 0.320 and 0.115 ppm dw; 2) Southern California Bight, 0.235 and 0.088; 3) Gulf Coast of Florida, 0.212 and 0.028; and 4) Texas Coast, 0.009 and 0.005 (Table 15.2).

Mean and median *fine-grained normalized* sediment PCB concentrations at 18 NS&T sites in the Southern California Bight were also comparable to concentrations at 7 sites in Long Island Sound (0.226 and 0.204 ppm dw), but higher than in 8 Puget Sound sites (0.142 and 0.051 ppm dw), or 5 San Francisco Bay sites (0.099 and 0.068 ppm dw), and nearly 5 times higher than 8 Chesapeake Bay sites (0.055 and 0.044 ppm dw; Table 15.2). Compared to the Hudson Raritan Bay area near New York (5 sites, mean 0.582 and median 0.642 ppm dw), mean and median PCB concentrations were only slightly lower in San Diego Harbor (0.404 and 0.328 ppm dw) and Los Angeles-Long Beach harbors (0.254 and 0.206 ppm dw) (Table 15.2). Thus, while there are large areas of the Bight with apparently low concentrations of PCBs in sediments (less than 0.001 ppm dw), concentrations in harbor areas of Los Angeles and San Diego are high enough to make the regional average comparable to averages in urban embayments of the northeast United States. The overall non-normalized mean level of tPCBs in sediment measured by the NS&T Program between 1984 and 1989 was low: 0.085 ppm dw (median, 0.018 ppm dw).

PCBs currently found in sediments from several areas in the Southern California Bight may be at concentrations toxic to sensitive marine invertebrates or their larvae. In a review of data from both acute and chronic toxicity tests, Dexter and Field (1989) found that lethal and sublethal effects and apparent thresholds were reported in the range of 0.1 to about 4.0 ppm dw. In addition, Swartz *et al.* (1988) reported a 10-day LC_{50} (concentration lethal to one-half the test organisms) of 10.8 ppm ww (9.8 to 11.0) for the infaunal amphipod, *R. abronius*. The median concentration for all these tests falls in the range of 0.1 to 1.0 ppm dw. Both authors caution that toxicity decreased dramatically with increasing concentrations of TOC (which also occurs frequently in PCB contaminated areas such as near sewage outfalls). This concentration range (0.1 to 1.0 ppm dw) has apparently never been approached or exceeded at offshore islands, the San Pedro Basin, in rural coastal areas of the open coast, in Upper Newport Bay, or at the Point Loma sewage discharge site. Historically (in the 1970s), sediment PCB concentrations have exceeded 0.1 ppm dw at some sites in Santa Monica Bay, off Palos Verdes, near the Orange County outfall, in Los Angeles-Long Beach harbors, and within San Diego Harbor. By the mid-1980s, concentrations were below this at most outfall area stations, but recent surveys have been inadequate to confirm that concentrations throughout major harbors are also below 0.1 ppm dw; clearly, however, specific harbor sites sampled by NOAA (Varanasi *et al.*, 1989; McCain *et al.*, 1989) are above this possible toxic level of 0.1 ppm dw.

Long and Morgan (1990) determined that the range of sediment PCB levels associated with adverse biological effects range from 0.003 ppm to 1140 ppm dw. The tenth percentile (ER-L) occurred at 0.05 ppm and the median value was 0.4 ppm dw (ER-M). Areas where sediments have exceeded 0.4 ppm include San Diego Harbor, Palos Verdes, Santa Monica Bay, and Los Angeles-Long Beach harbors. Many bays and outfall areas have yielded sediments containing 0.05 ppm dw.

Table 15.2. Summary of tPCB concentrations, mg/kg (ppm) dw, in fine-grained sediments from the entire U. S. coastline, from three ocean areas, and from ten subregions. Concentrations are normalized to fine-grain content; computed from NS&T Benthic Surveillance Project (1984 and 1985) and data from the Mussel Watch Project (1986 and 1987) as cited in NOAA (1988).

SITE	Number of site means	Mean	Median	Minimum	Maximum	Standard Deviation
United States	172	0.147	0.036	0.0015	2.288	0.306
Atlantic Coast	58	0.243	0.113	0.0015	2.063	0.350
Mid-Atlantic Bight	30	0.320	0.115	0.033	2.063	0.397
Long Island Sound	7	0.226	0.204	0.123	0.460	0.113
Hudson/Raritan Bay	5	0.582	0.642	0.204	0.755	0.227
Delaware Bay	5	0.123	0.069	0.035	0.364	0.136
Chesapeake Bay	8	0.055	0.044	0.003	0.125	0.055
Gulf of Mexico Coast	62	0.071	0.012	0.002	2.288	0.269
Florida	18	0.212	0.028	0.005	2.288	0.535
Texas	22	0.009	0.005	0.002	0.053	0.011
Pacific Coast	44	0.149	0.054	0.005	0.977	0.247
Northwest Coast	8	0.020	0.018	0.005	0.044	0.012
Puget Sound	8	0.142	0.051	0.010	0.902	0.287
San Francisco Bay	9	0.099	0.068	0.031	0.400	0.114
Southern California Bight	18	0.235	0.088	0.017	0.977	0.304
San Diego Harbor	3	0.404	0.328	0.017	0.867	0.403
Los Angeles-Long Beach harbors area [1]	5	0.254	0.206	0.049	0.328	0.142
South Coastal [2]	5	0.039	0.026	0.020	0.073	0.023
North Coastal [3]	3	0.087	0.103	0.043	0.115	0.039

[1] Anaheim Bay to San Pedro
[2] Point Loma to Newport Beach
[3] Santa Monica Bay to Santa Barbara

Long-term trends of PCB accumulation in sediments in the Southern California Bight are suggested from results of the analysis of one dated core taken from anaerobic sediments in the Santa Barbara Basin in 1970 (Hom et al., 1974). Concentrations of tPCBs rose from below an analytical detection limit of 0.02 ppm dw (before 1945) to 0.05 ppm dw by 1952 and then to 0.103 ppm dw by 1967. Unfortunately there have been no recent dated cores from this site to confirm that concentrations have since declined.

Both long-term and recent shorter term trends of sediment PCB contamination are available from cores and repeated surface sediment grabs taken along the Palos Verdes shelf by CSDLAC (Stull et al., 1988). Core profiles indicate that PCB concentrations rose and then fell. Maximum concentrations are now about 10 centimeters below the sediment surface. Four surface sediment surveys along the 60-m isobath off Palos Verdes indicate that mean tPCB concentrations at seven comparable sites fell about 3-fold from 1.48 ppm dw in 1973 to 0.53 ppm dw in 1988 (CSDLAC, unpublished data, Figure 15.5). By comparison, PCB mass emissions from the CSDLAC outfalls at Palos Verdes decreased more than 99 percent from 1280 kg in 1973 to 80 kg in 1985 and below detection (apparently less than 80 kg) in 1986, 1987, and 1988 (SCCWRP, 1987a, 1988, and 1989). The rate of decline of PCBs in surface sediments off Palos Verdes is much slower than the rate of decline of PCB input from the adjacent outfalls.
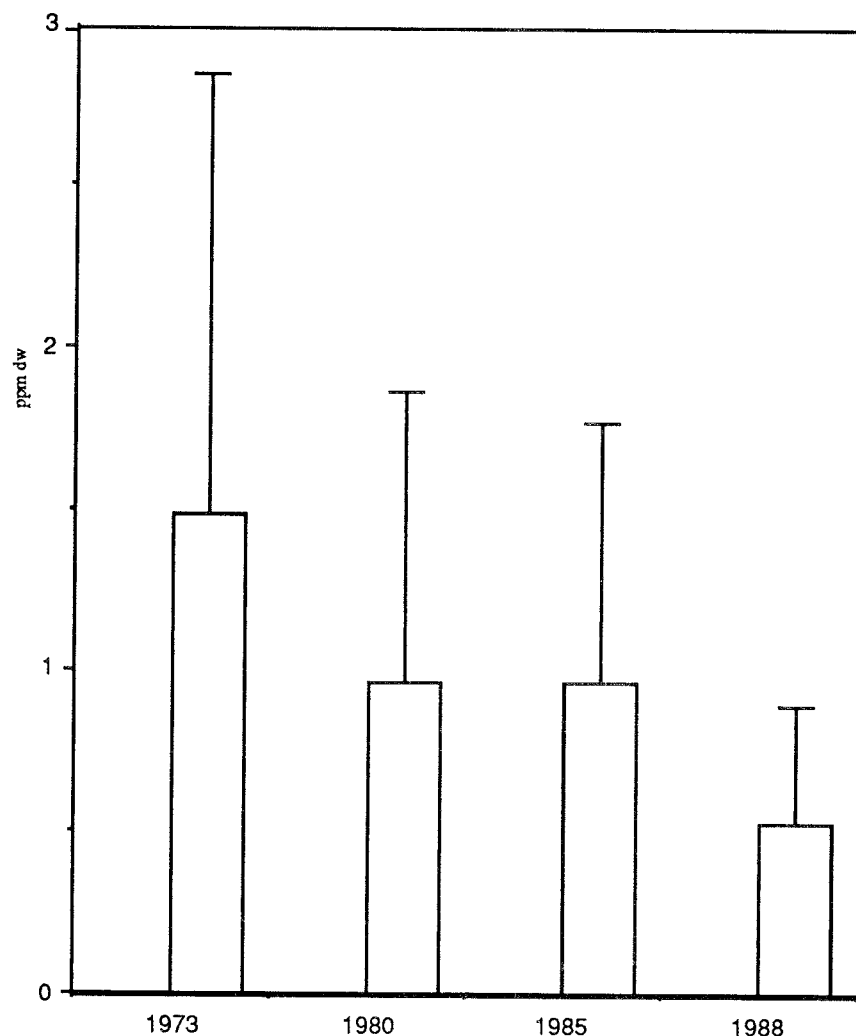
Figure 15.5. Mean ± standard deviation of tPCB concentrations in surface sediments at seven stations along the 60-m isobath at Palos Verdes, 1973 to 1988. Computed from unpublished data CSDLAC.

In summary, sediments of the Southern California Bight mainland shelf have contained PCBs at concentrations comparable to those in urban areas of the Northeast Coast. However, concentrations decline sharply away from several epicenters; mainly the Los Angeles-Long Beach harbors area including Palos Verdes (for example San Pedro Bay) and San Diego Harbor. Concentrations above 0.5 ppm dw were generally restricted to deep water off the Palos Verdes shelf near the CSDLAC outfall and along the eastern shoreline of northern and central San Diego Harbor. Concentrations between 0.05 and 0.5 ppm dw were common in the Los Angeles-Long Beach harbors area including Long Beach and Seal Beach and in the offshore south and central area of Santa Monica Bay. These are potentially toxic concentrations (Dexter and Field , 1989) and could lead to toxic effects in marine life. Concentrations between 0.025 and 0.05 ppm dw occurred in scattered locations between Seal Beach and Dana Point, at a few sites northwest of Santa Monica Bay, and at inshore areas of Santa Monica Bay. Concentrations between 0.01 and 0.025 ppm dw were common along the mainland shelf between Santa Barbara and Dana Point (outside the areas mentioned above). The cleanest area of the mainland shelf was the coast of San Diego County with concentrations generally in the range of 0.002 to 0.010 ppm dw. Concentrations in the San Pedro Basin were comparable to those of coastal San Diego County. The PCB concentrations in sediments near offshore islands were the

lowest measured (all below 0.001 ppm dw). Data to determine recent long-term trends in sediments are limited to a few outfall sites where concentrations have been decreasing during the past 10 to 15 years.

PCBs IN MUSSELS

Concentrations of PCBs in body tissues of resident mussels collected at sites in the Southern California Bight show broad patterns of occurrence that are similar to those for sediments. Locations near the Palos Verdes Peninsula, in Los Angeles-Long Beach harbors, Newport Bay, and in San Diego Harbor showed higher concentrations than the other southern California sites sampled. In addition, intensive surveys have identified local-scale gradients of PCB contamination within harbors and marinas, including the locations of some "hot spots" of PCB contamination.

Although the NPMP monitored organochlorine compounds in mussels from three sites in the Southern California Bight (Mugu Lagoon, Anaheim Bay, and Hedionda Lagoon) monthly from 1965 to 1971 (Butler, 1973), PCBs were not explicitly reported until the sites were resurveyed in 1977. At that time, concentrations were below the 0.01 ppm ww detection limit (Butler et al., 1978). Since 1971, there have been four periods of one or more years during which PCBs were measured in resident mussels on a regionwide basis. In 1971, a survey of Aroclor 1254 in coastal mussels (M. californianus) at 24 California sites included 20 located between Gaviota, California and Punta Banda, Baja California (SCCWRP, 1973). The most intensive sampling during the past 20 years occurred in 1974 when SCCWRP surveyed 75 sites including 24 between Palos Verdes and Seal Beach (including Los Angeles-Long Beach harbors), 13 in and near Newport Bay, 19 in and near San Diego Bay and Harbor (Young et al., 1975; McDermott et al., 1975), and 19 open-coastal and island sites (Young and Szpila, 1975; deLappe et al., 1980). Five open coastal sites and nine sites in Los Angeles-Long Beach and San Diego harbors, were sampled in 1976 as part of the nationwide U.S. EPA Mussel Watch (Farrington et al., 1982); five coastal sites were also sampled in 1977. In 1977 and 1978, the CMW sampled resident M. californianus at up to 13 coastal and island sites each summer and fall (Risebrough et al., 1980). Coincidentally, Gutierrez-Galindo and Cajal-Medrano (1981) measured PCBs in resident and transplanted mussels at up to eight sites in Baja California. Together, the 1977 surveys extended from Point Conception south to Bahia de San Quintin (400 km). The CMW maintained annual monitoring at the coastal sites (Oceanside and Royal Palms) through the 1980s and conducted numerous "intensive" surveys in bays and harbors, but did not repeat the broad 1977-78 survey cycle. A survey occupying some of the historic southern California sites was conducted in 1985 by Risebrough (1987). Beginning in 1986, the NOAA NS&T Program began annual sampling of mussels at 16 sites including 11 coastal sites (M. Californianus) and 5 bay or jetty sites (M. edulis).

The SCCWRP and CMW programs and the Mexican programs, reported PCBs in terms of one or more Aroclors (Aroclor 1254 always reported); whereas, the early NS&T Program results are reported by chlorination number. In addition, some investigators (McDermott et al., 1975; Gutierrez-Galindo and Cajal-Medrano (1981) reported data only in terms of wet weight (NOAA, 1989; deLappe et al., 1980; Risebrough et al., 1980). The CMW Program reports wet weight, dry weight, and lipid-normalized concentrations. The reader is therefore cautioned to observe units before comparing the data presented below. For some comparisons cited in the text, wet weight-based data was multiplied by 5.0 to obtain estimated dry weight concentrations.

Four surveys have produced data useful for establishing the broad range of PCB concentrations in mussels of the Bight. In the 1971 SCCWRP survey, concentrations of Aroclor 1254 ranged from 0.014 ppm ww at a site on Anacapa Island to 0.520 ppm ww at Royal Palms on the Palos Verdes Peninsula (Figure 15.6). These are approximately equivalent to a dry weight range of 0.07 to 2.60 ppm as cited in Risebrough et al. (1980). In addition to the values shown in Figure 15.6 is a concentration of 0.016 ppm ww (about 0.08 ppm dw) for a sample collected at Punta Banda near Ensenada (SCCWRP, 1973). The regional distribution of PCBs in mussels resembled that for tDDT in the same study (chapter 16) in that concentrations declined with distance in any direction from Los Angeles. Total PCBs appear to be higher south of Palos Verdes than to the north. Thus, the mean Aroclor 1254 concentration for four stations from Point Dume to Gaviota was 0.07 ppm ww whereas for four stations from Newport to Point Loma, it was 0.114 ppm ww. By comparison, the four intermediate Los Angeles-area stations had a mean of 0.326 ppm ww and the seven islands, 0.031 ppm ww.

SCCWRP measured Aroclor 1254 in M. californianus at coastal sites in the summer of 1974 and found the distribution of concentrations different from 1971 (Figure 15.7). Concentrations of Aroclor 1254 for the 16 locations represented in Figure 15.7 ranged from 0.006 ppm ww at San Nicolas Island to 0.370 ppm

ww at Port Hueneme. While body burdens at Point Vicente and Royal Palms, on the Palos Verdes Peninsula (0.104 and 0.140 ppm ww, respectively) were elevated relative to most other sites, the concentrations at these sites declined by approximately a factor of four between 1971 and 1974. Decreases were also apparent at other sites.

Risebrough *et al.* (1980) and deLappe *et al.* (1980) provide PCB concentrations (presumably Aroclor 1254) on a dry weight basis and included three additional sites not shown in Figure 15.7 (Seal Beach, Newport Jetty, and Oceanside). For all 19 coastal sites sampled in 1974, PCB concentrations ranged from 0.020 ppm dw at a site on the northwest coast of Santa Catalina Island to 1.60 ppm dw at both Port Hueneme and Royal Palms. Using mean concentrations, the difference between sites to the north and south of Palos Verdes was not as notable as in 1971. However, using the median for each coastal sector, it was. The means for six north-coast sites and four south-coast sites were 0.322 and 0.263 ppm dw, respectively; whereas, the medians were 0.080 and 0.215 ppm dw, respectively. Three sites in the Los Angeles area had a mean and median of 0.983 and 0.620 ppm dw, respectively.

As part of the CMW, Risebrough *et al.* (1980) continued synoptic surveys of PCBs in *M. californianus* at 12 coastal and island sites in the Bight during the summers and winters of 1977 and 1978. Large-scale patterns were similar to those seen in 1971 and 1974 with lower concentrations during 1977 and 1978, except at San Miguel Island. It was postulated that PCBs were being recycled into mussels from PCB-contaminated pinniped excrement from nearby haul-out areas (Figure 15.8).

Also during late 1977 and early 1978, Gutierrez-Galindo and Cajal-Medrano (1981) measured Aroclor 1254 monthly in resident *M. californianus* from four sites in Baja California, thus effectively extending information along nearly the entire 400-km coast of the Bight. The CMW data (July and December, Risebrough *et al.*, 1980) were converted to a wet weight basis and compared to the September and November data of Gutierrez-Galindo and Cajal-Medrano (1981). As shown in Figure 15.8, mean concentrations of Aroclor 1254 increased over 10-fold from Point Conception eastward to Royal Palms (Palos Verdes) then progressively decreased 100-fold southwest to Punta China and Erendira in Baja California.

While numerous local surveys of PCBs in mussels were conducted during the late 1970s and 1980s by the CMW, synoptic surveys were not conducted again until 1986-88 by the NOAA NS&T National Mussel Watch Project. Data for 1986 (Figure 15.9) agree with the patterns observed in 1971-78 with highest concentrations at harbor stations (San Pedro Bay and San Diego Bay) and intermediate to low concentrations at coastal and island sites. However, unlike other synoptic sampling efforts, the NS&T Mussel Watch results showed a concentration of high values in the southern portion of the Southern California Bight between La Jolla and San Diego. Mean concentrations that year ranged 32-fold from 0.064 ppm dw in samples from an Oceanside jetty site to 2.064 ppm dw at a site on Harbor Island in San Diego Harbor.
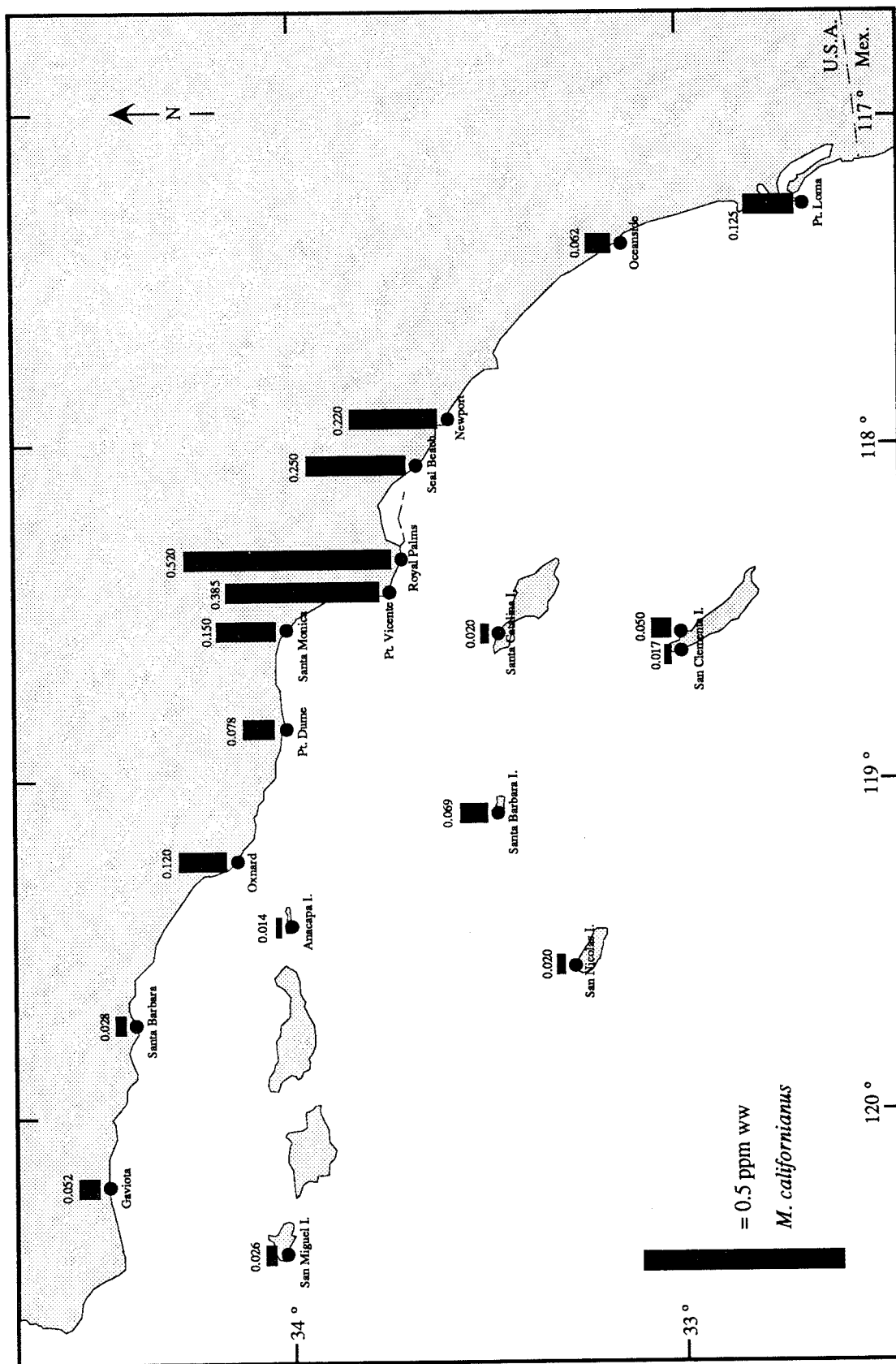
Figure 15.6. PCB (Aroclor 1254) in soft body tissue of mussels sampled in 1971. Values shown are means of six samples, each sample equals one individual. Source: Young, 1974.
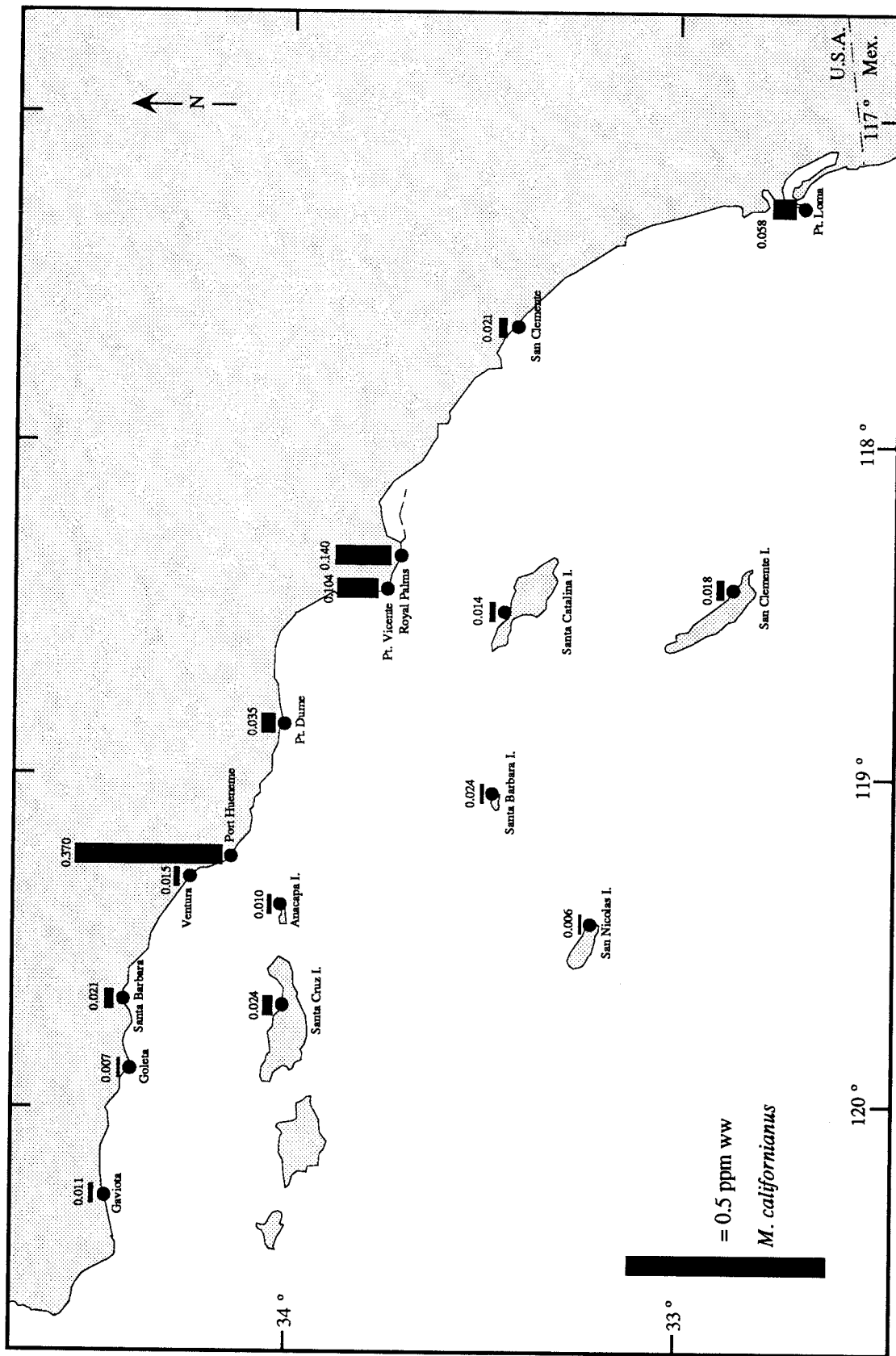
Figure 15.7. PCB (Aroclor 1254) in soft body tissue of mussels sampled in the Southern California Bight in 1974. Source: Young and Szpila, 1975.
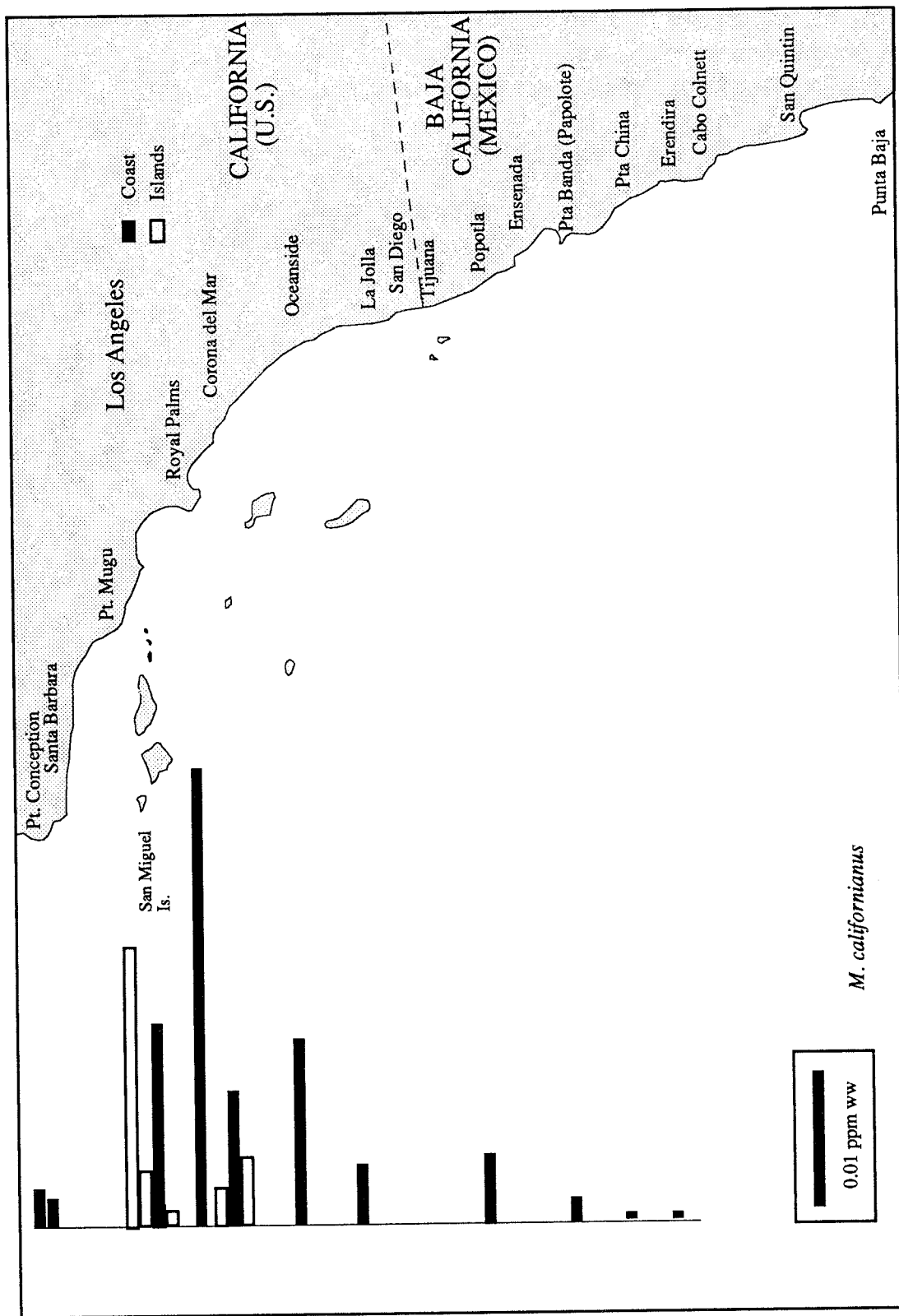
Figure 15.8. Average Aroclor 1254 concentrations (ppm ww) in mussels from Southern California (deLappe et al, 1980) and Baja California(Gutierrez-Galindo and Cajal-Medrano, 1981) during summer and fall, 1977.
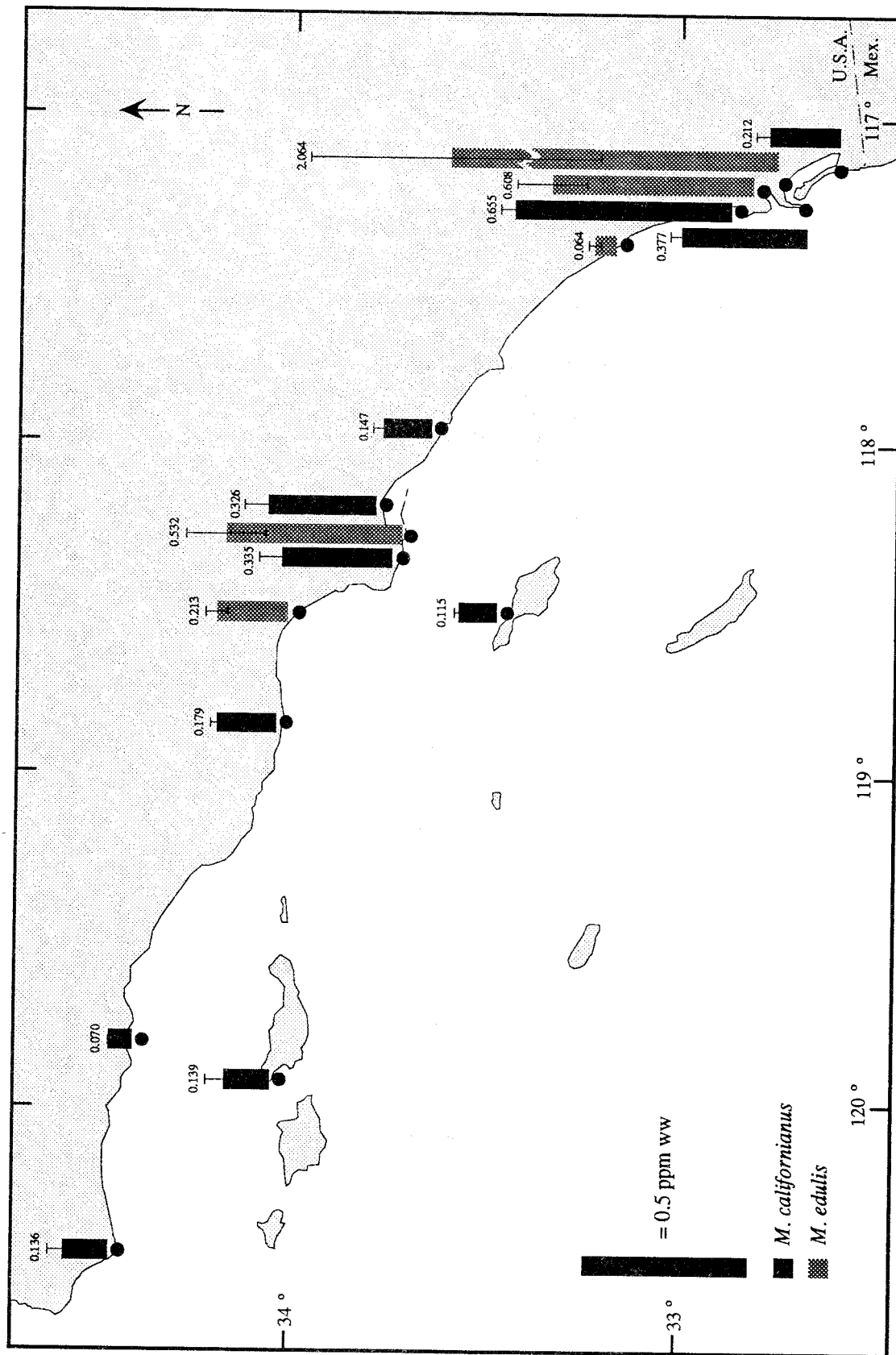
Figure 15.9. tPCB in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

As noted above, harbors as well as the open coast were surveyed in 1974 for Aroclor 1254 in mussels. Overall, concentrations of Aroclor 1254 on a computed dry weight basis, ranged from 0.006 ppm dw in *M. californianus* from an island site to 5.82 ppm dw at a site in San Diego Harbor (Table 15.3). Mean concentrations in ppb wet weight are also shown in Figure 15.10 for three harbors, the islands, and the mainland coast. Areawide mean concentrations were 4 to 12 times higher along the mainland coast compared to island sites. By contrast, samples of *M. edulis* from inside harbors, had area-mean PCB concentrations ranging from 1.21 ppm dw in the San Pedro Bay area to 2.23 in San Diego Harbor. These area-wide mean concentrations were 3 to 7 times higher than concentrations in mussels from nearby open coastal sites sampled at the same time, and 30 to 60 times higher than concentrations found in *M. californianus* from the island sites sampled the previous winter. Among harbors, mussels in San Diego Harbor were about twice as contaminated with PCBs (2.23 ppm dw) as mussels from San Pedro Bay sites (1.21 ppm dw; Table 15.3). Thus during 1974, there was a 30- to 60-fold concentration gradient of PCBs in mussels from highest concentrations in harbors to lowest at the offshore islands.

Table 15.3. **Comparison of PCB concentrations in mussels among three harbors, the mainland coast, and island sites sampled in 1974. Collected from three harbors (and respective "outside" reference sites) in summer and fall of 1974 and from 14 mainland and 6 island sites sampled in January 1974. Concentration converted to dry weight from published values by multiplying by wet weight concentrations x 4.48. Source: McDermott *et al.*, 1975.**

	N	ppm dw Mean	Range	Median
San Pedro Bay [1,3]				
Inside	22	1.21	0.36 - 2.51	0.85
Outside	2	0.74	0.67 - 0.81	0.74
Newport Bay [2,3]				
Inside	11	1.56	0.36 - 5.38	1.25
Outside	2	0.45	0.22 - 0.67	0.45
San Diego Bay [3]				
Inside	14	2.23	0.31 - 5.82	1.99
Outside	5	0.31	0.18 - 0.45	0.32
Mainland Coast [4]		0.44	0.02 - 1.60	0.17
North	6	0.32	0.02 - 1.60	0.08
Los Angeles	3	0.89	0.46 - 1.60	0.62
South	4	0.26	0.09 - 0.53	0.22
Islands [4]	6	0.052	0.006 - 0.11	0.03
Overall	75	----	0.006 - 5.82	----

[1] From San Pedro west to Anaheim Bay, including sites in Los Angeles-Long Beach harbors, Alamitos Bay, and Anaheim Bay.

[2] Lower Newport Bay, only.

[3] *Mytilus edulis*, summer, fall 1974
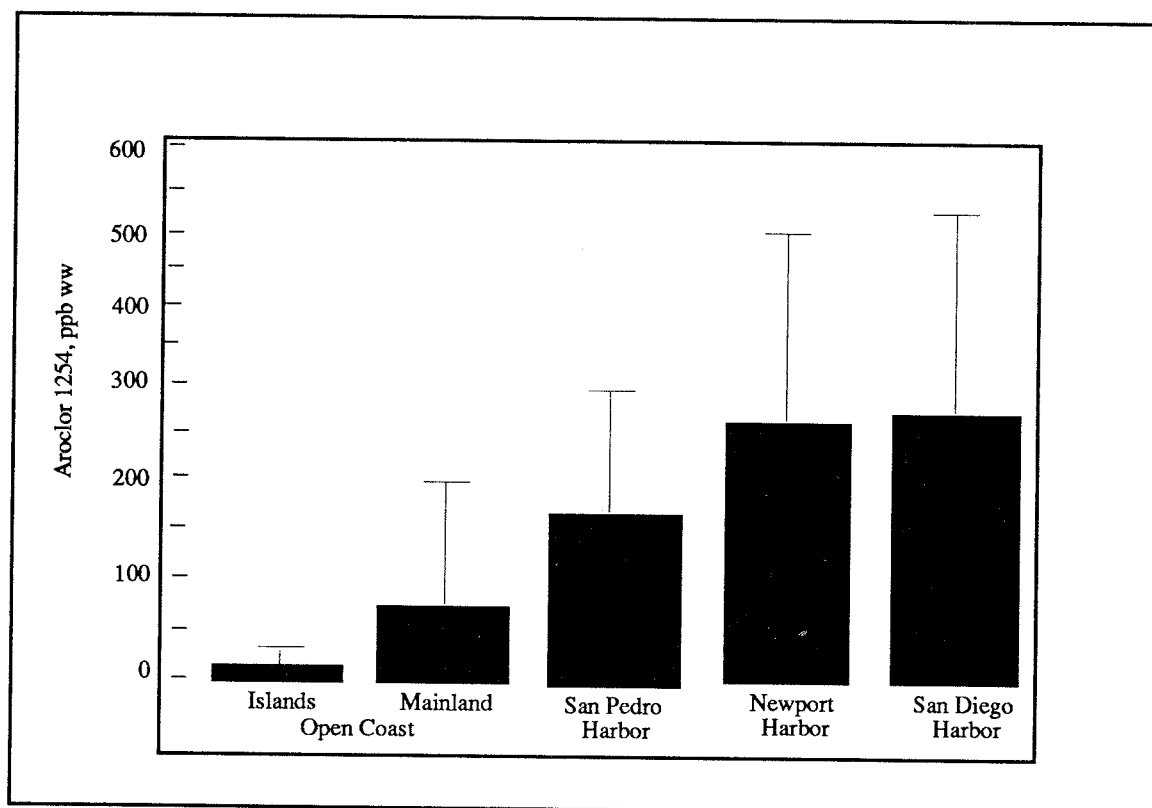
[4] *Mytilus californianus*, winter 1974.

Figure 15.10. Concentrations (mean and standard deviation) on wet weight basis, PCBs in mussels from five coastal and harbor collections make in 1974 (from McDermott *et al.*, 1975). Corresponding values are given in Table 15.3.

Where sampling has been sufficiently intense, concentrations of PCBs in *M. edulis* have been 5 to 10 times higher in back reaches than near bay and harbor entrances. In the San Pedro Bay (Los Angeles-Long Beach harbors) area, concentrations in 1974 increased from the breakwater (0.12 to 0.43) inward to the inner harbor area (0.42 to 0.56 ppm ww) but there were notable exceptions (Figure 15.11). Indeed, one of the lowest concentrations (0.14 ppm ww) was in a Long Beach Harbor channel whereas the highest (0.81 ppm ww) was not in the main harbor area, but in Alamitos Bay near the Long Beach Marina (Figure 15.11). In San Diego Harbor during 1974, PCB concentrations in *M. edulis* increased abruptly from 0.06 ppm ww at Point Loma to 0.50 ppm ww at the entrance (Figure 15.12). Concentrations were generally high along the north and east shore of San Diego Harbor (0.21 to 1.31 ppm ww) but at two sites deep inside the bay along the isthmus, concentrations (0.07 and 0.12 ppm ww) were only slightly higher than at Point Loma and an adjacent coastal site (0.06 and 0.10 ppm ww, respectively; Figure 15.12). In Newport Bay (not shown), PCB concentrations increased from the range of 0.05 to 0.16 ppm ww at six open coastal and entrance sites to 0.46 to 1.20 ppm ww at three sites deep inside the bay. The fact that PCB concentrations in Newport mussels were comparable to those from Los Angeles-Long Beach and San Diego is surprising in that no point sources had been identified and the degree of industrialization was considerably less than at the urban embayments. While such gradients may identify possible sources, they may also simply reflect accumulations resulting from poor water exchange. Using transplanted mussels, the CMW Program has conducted additional intensive surveys of PCBs in these and other bays and harbors. Although this review excludes these data, they are extremely important in identifying possible point and nonpoint sources and should be reviewed for regulatory purposes.
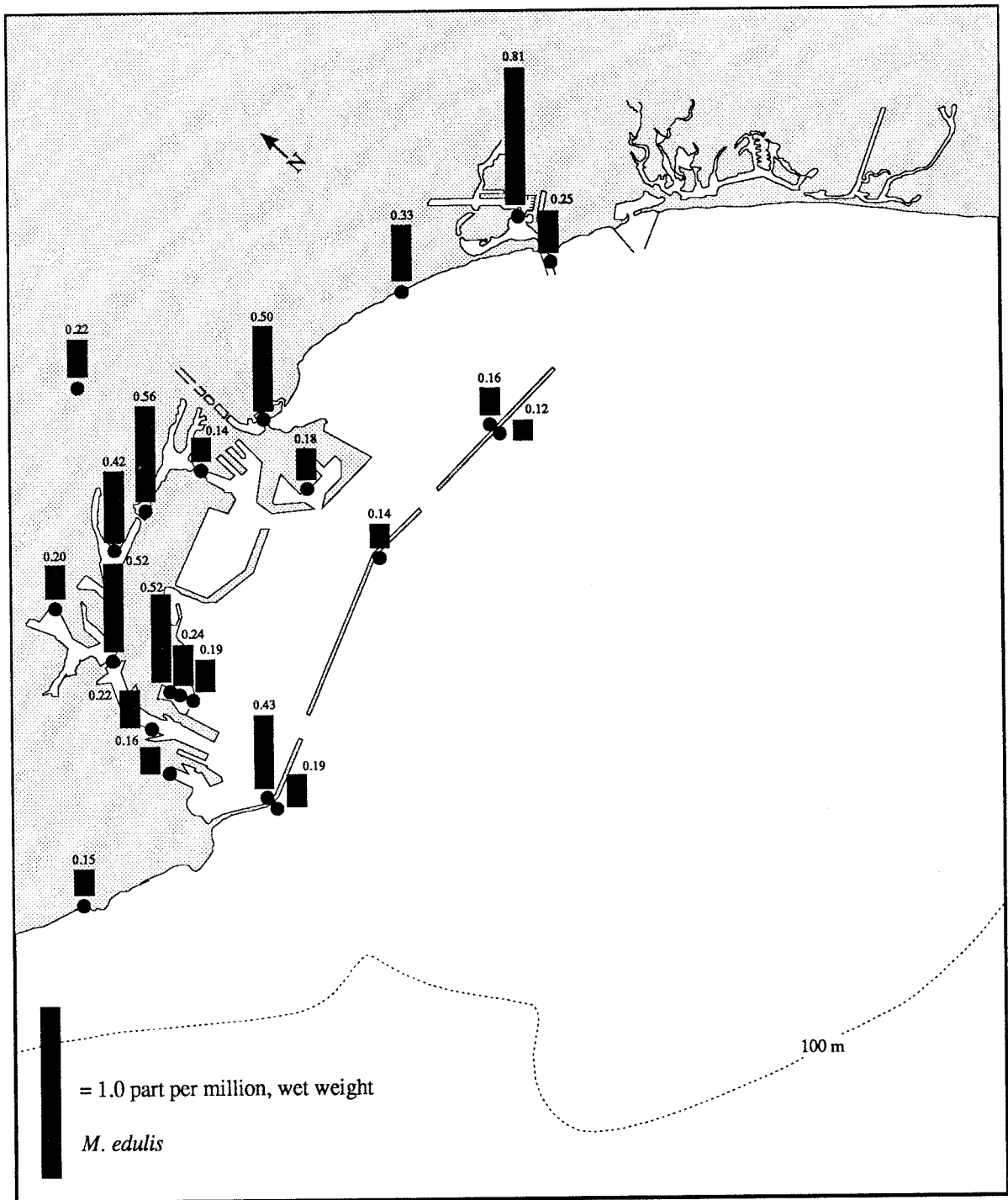
Figure 15.11. Total PCBs in mussels, sampled in San Pedro Bay in 1974. Source: McDermott *et al.*, 1975.

Figure 15.12. Total PCBs in mussels sampled in San Diego Harbor in 1974. Source: McDermott *et al.*, 1975.

The overall mean levels of tPCBs in mussels sampled at all sites by NOAA's NS&T Program between 1986 and 1989 are low. The mean concentration is higher in *M. edulis* (0.731 ppm dw) than in *M. californianus* (0.109 ppm dw). Median values were approximately half overall mean values: 0.376 ppm dw in *M. edulis* and 0.065 ppm dw in *M. californianus*.

Temporal Trends

Before initiating the NOAA NS&T Mussel Watch Program in 1986, only two sites (Oceanside and Royal Palms at Palos Verdes) were monitored yearly for the specific purpose of determining long-term trends. However, mussels from other sites were sampled frequently enough during the past 15 to 20 years to help establish long-term trends elsewhere.

Long-term trends of PCBs in mussels in southern California are best portrayed by results from two separate studies; one sponsored by the LARWQCB (Risebrough, 1987) and the other a part of the CMW Program. Figure 15.13 illustrates concentrations of tPCBs measured between 1971 and 1986 in *M. californianus* collected at Royal Palms and on Santa Barbara Island, as reported in Risebrough (1987). Concentrations found in mussels collected on Santa Barbara Island were approximately an order of magnitude less than those from Royal Palms mussels. However, with the exception of a relatively low tissue concentration measured in 1972 on Santa Barbara Island, considerably higher levels of t PCBs were found in early (1971 to 1974) collections and low levels occurred between 1977 and 1986.
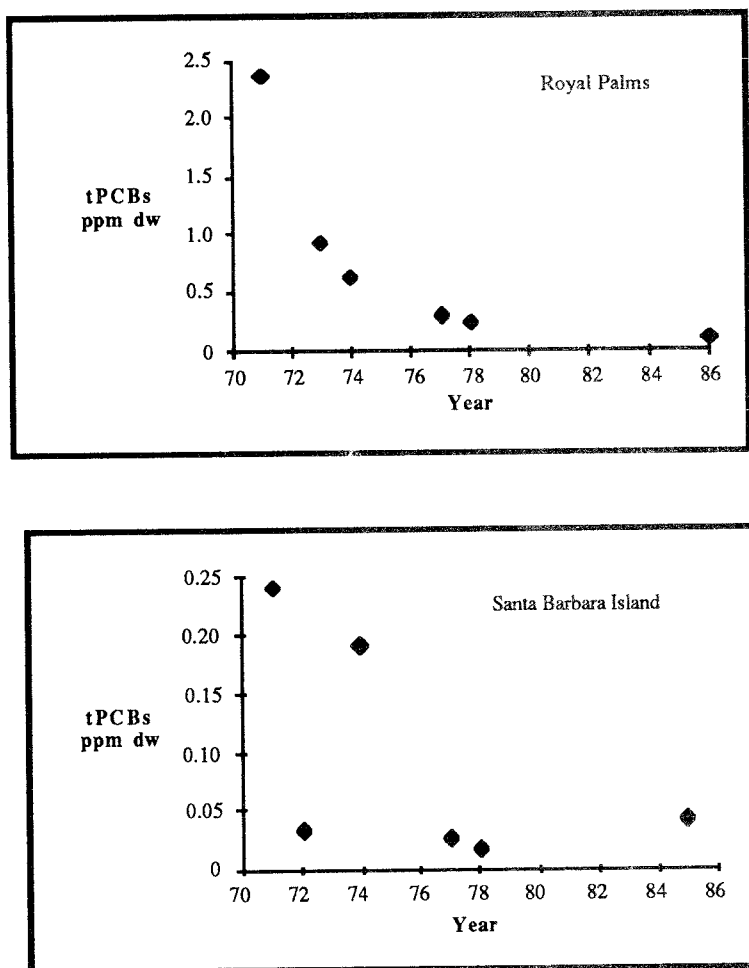

Figure 15.13. **Concentrations of tPCB in** *M. californianus* **collected at Royal Palms and Santa Barbara Island 1970-86. Source: Risebrough, 1987. Note scale differences.**

No data were reported by Risebrough (1987) for the period between 1978 and 1985. However, this is a time period well covered by the CMW Program. Results from CMW long-term reference sites at Royal Palms and at Oceanside are shown in Figure 15.14. Although values at Royal Palms were about twice those at Oceanside measured at about the same periods of time, the general temporal trends over the entire measurement period of 1977 to 1985 were similar. With the exception of one or two relatively high concentrations between 1980 and 1981, values were fairly consistent between 1978 and early 1985, ranging between 0.15 and 0.32 ppm at Royal Palms and between 0.05 and 0.13 ppm at Oceanside. The steep declines from the early 1970s to the late 1970s that were shown in Risebrough's results apparently did not continue into 1982, or at least were not as evident in mussel tissue concentrations from the latter period. The anomalous CMW concentrations in 1980 and 1981 were about double the values in late 1979 at Royal Palms and Oceanside. Measurements made in late 1985 at both sites represented minimum values obtained (0.06 ppm at Royal Palms and below detection limits at Oceanside).

Results from the NS&T Program showed significant declines in tPCB between 1986 and 1988 at five sites in southern California--Point Loma, Santa Catalina Island, Santa Cruz Island, Point Santa Barbara, and Point Conception (NOAA, 1989). PCBs at other sites were variable or showed decreases that were not significant. The only site where PCBs increased was Anaheim Bay where the increase was not significant. Grouping results by site type showed declines for most areas (Table 15.4).
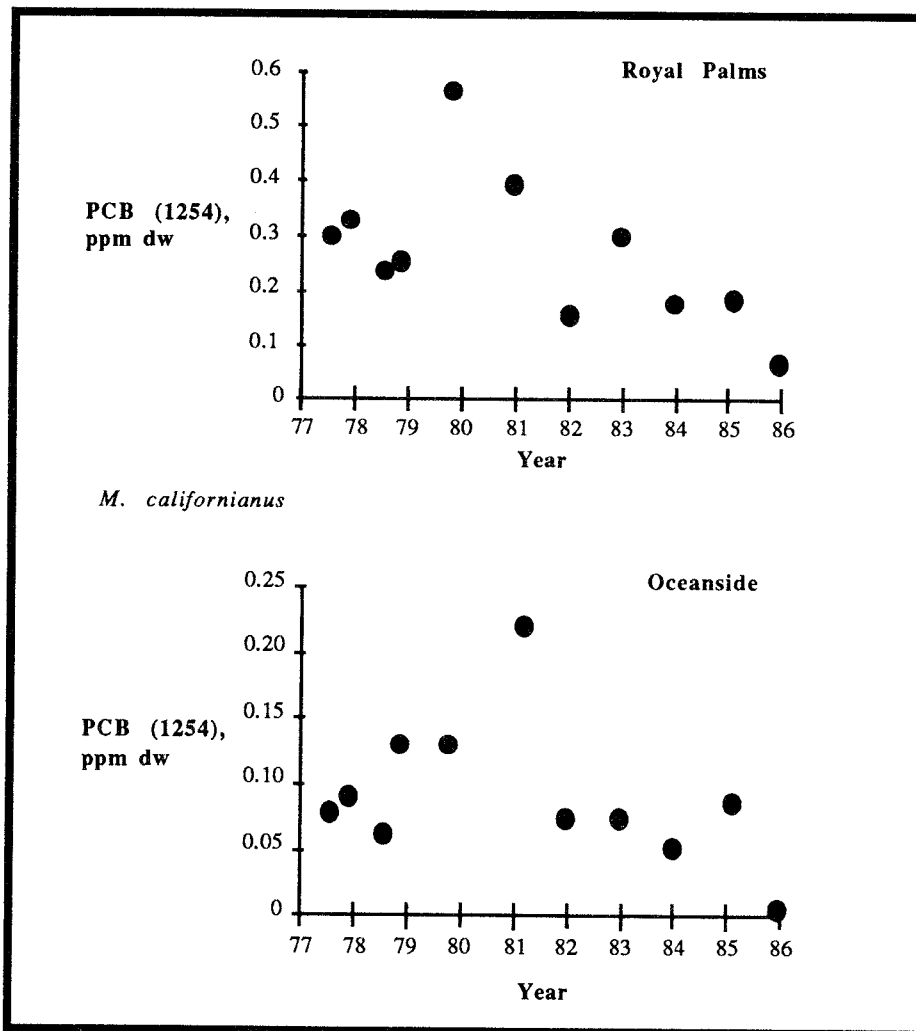

Figure 15.14. Temporal trends of PCB (Aroclor 1254) in soft body tissues of mussels sampled 1977 to 1985 at Royal Palms and Oceanside4 sites. Note scale differences. Source: Phillips, 1988.

Table 15.4. Changes in overall concentrations of PCBs in mussels from the Southern California Bight between 1986 and 1988 as measured in NOAA's NS&T Program (NOAA, 1989).

Area	Number of Sites	Median concentration, ppm ww			
		1986	1988	Percent of 1986	Percent Decrease
Islands[a]	2	0.125	0.017	6	86
Open Coastal [a]	7	0.210	0.085	40	60
Bays and Harbors					
M. californianus	5	0.530	0.270	51	49
M. edulis	2	0.240	01.415	172	0

Together, data from these frequently monitored sites (Royal Palms, Oceanside, and Santa Barbara Island) suggest that PCB concentrations in mussels of the Bight have generally decreased over the past 10 to 20 years. Additional data from a few synoptic surveys seem to bear this out. Young and Szpila (1975) reported that the median percent decrease (median of paired differences) of Aroclor 1254 at 13 of the island and coastal sites through the Bight between 1971 and 1974 was 31 percent; the actual 13-station median concentrations were 0.052 ppm ww in 1971 and 0.021 ppm ww in 1974 (for a median concentration decrease of 60%).

If, as was suggested by the 1971 results, primary local sources of PCBs to mussels were the nearby outfalls, it might be expected that the apparent decrease observed by SCCWRP and by de Lappe et al. (1980) in Palos Verdes mussels would be preceded by declines in PCB mass emissions from treatment plants. In fact, Figure 15.1 illustrates that total mass emissions of PCBs from all municipal discharges into the Southern California Bight (of which the four near Palos Verdes comprised 88% of the total flow) did show a substantial decline between 1971 and 1973, from 8730 and 9830 mt of total PCB in 1971 and 1972 to 4620 mt in 1973 (Mitchell and McDermott, 1975). This roughly corresponds to the decrease of PCB contamination of mussels at Royal Palms.

However, a regionwide comparison of reported mass emissions of PCBs from seven southern California municipal wastewater dischargers with concentrations of PCBs measured in *M. californianus* tissue at the CMW Program reference sites did not indicate a significant relationship at ($\alpha = 0.05$) between waste water emissions and PCB concentrations in mussels at nearby sites. The nonparametric statistic, Spearman's rank correlation procedure, was used to evaluate the relationship between annual discharge levels and tissue concentrations of PCBs. At Royal Palms, $r_s = 0.25$, at a significance level of 0.589 and at Oceanside, $r_s = 0.29$, at a significance level of 0.535.

These results suggest that (with the exception of Palos Verdes in the early 1970s) municipal discharges of PCBs were not important in determining tissue concentrations as was previously indicated by results from SCCWRP sampling. This may reflect the proportionally greater contribution of nonpoint sources of PCBs, possibly including dry aerial fallout.

PCBs IN FISH AND OTHER SPECIES

Analyses for concentrations of PCBs in fish have focused primarily on two tissues, muscle and liver. Muscle tissue presents an obvious human health concern, because it is the portion of the fish ordinarily eaten. Fish liver, while not normally consumed by humans, is the organ that bears a substantial burden of the metabolism of toxic materials. The liver also contains a relatively higher proportion of lipids, with which PCBs tend to associate. Therefore, contaminant burdens in muscle tissue bear a number of implications from a public health perspective; while liver tissue may be the best indication of the effects on the fish itself.

There is a large amount of data on concentrations of PCBs in fish and macroinvertebrates of the Bight. A conservative estimate is that there is data from over 5000 samples representing over 100 species. Several studies, such as the 1985 LARWQCB survey of organochlorines in kelp bass, black perch, and white croaker (Risebrough, 1987) and a 1981 USC-SCCWRP seafood survey of PCBs and DDT in white croaker and other sportfish (Gossett et al., 1982; 1983a) allow large geographic comparisons across major regions of the Bight, but such studies are rare and have not been repeated. Likewise, several studies at specific locations (mainly Palos Verdes) allow fairly easy reconstruction of PCB time-series trends for periods of up to 15 years. Examples include a 1971-82 time series for Dover sole at Palos Verdes (Young, Gossett, and Heesen, 1988) and a similar time series for kelp bass, black perch, and Dover sole at Palos Verdes (Smokler et al., 1979; CSDLAC, unpublished data). However, because of a continuing lack of continuity of the sites, species, tissue types, compositing techniques, and analysis methods among local, regional, state, and federal programs, there are no data that allow easy reconstruction of the history of PCB contamination in fish or macroinvertebrates of the Bight. From the great potpourri of published data, and even larger amounts of unpublished data, long-term regionwide trends of PCB contamination can be developed only with considerable effort. An additional limitation is that there are very few data from bays and harbors where sediment and mussel watch data suggest much of the PCB contamination originates.

Excluded from detailed review in this report are PCB data in fish from discharger monitoring programs and from recent and older one-time synoptic surveys. Unpublished data exist for over 50 species of fish and macroinvertebrates from monitoring programs performed by or on behalf of the Oxnard Treatment Plant, the Hyperion Treatment Plant, the CSDLAC, and the CSDOC (CSDOC, 1978 through 1987). Additional one-time historical surveys included measurements of PCBs in eight species of fish from Los Angeles Harbor and Santa Catalina Island collected in 1979 through 1981 reported by Gadbois and Maney (1983); quarterly sampling of five species of fish, 1973 through 1976 in Los Angeles Harbor, at Long Beach, and in Mission Bay by Butler and Schutzmann (1978); 1970 samples of six species of fish and macroinvertebrates near the Orange County outfall and at Laguna by Munson (1972); and 1969 through 1973 collections of commercial fish at various sites by Stout and Beezhold (1981) and Duke and Wilson (1971). It is likely that data from these studies could be used with more recent data to reconstruct PCB time series for additional species and sites.

Geographic Patterns

During the mid-1970s and early 1980s, PCB concentrations ranged from less than 0.001 ppm ww in adductor muscle of scallops (*Hinnites* spp.) from Santa Catalina Island, Point Dume, Dana Point, and Cortez Bank to a maximum of 14.8 ppm ww in a composite of spiny dogfish muscle from the Palos Verdes Peninsula (Table 15.5). Liver tissue has contained higher levels of PCBs: up to 162.072 ppm ww in Dover sole from Palos Verdes. Macroinvertebrates (mollusks, crustaceans) and coastal pelagic fish (anchovy, sardine, mackerel) have been found to be considerably less contaminated than nearshore fish (croakers), flatfish (Dover sole, sanddabs), and one species of shark. Concentrations in crustaceans (lobsters, crabs, prawns) have never exceeded the value of 0.98 ppm recorded in one collection of yellow crab from Palos Verdes in 1976 (Table 15.5). Mean tPCB concentrations in crustaceans have ranged from 0.004 ppm ww in shore crabs from Newport Bay to 0.369 ppm ww in yellow crabs from Palos Verdes in 1976.

Concentrations of tPCB in fish muscle have ranged from less than 0.001 ppm ww in a sanddab collected in 1975 from Dana Point to 14.815 ppm ww in spiny dogfish collected in 1981 off Palos Verdes. Mean concentrations among species collections ranged from 0.008 ppm ww in anchovy from several open coastal sites in 1980-81 to 3.166 ppm ww in the entire 1977 Dover sole collection from Palos Verdes and 2.78 ppm ww in a 1975 collection of white croaker from Palos Verdes (Table 15.5).

Table 15.5. PCBs (ppm ww) in edible tissues of marine organisms from the Southern California Bight.

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	SOURCE
Kelp	Los Angeles Harbor	1980	5	0.021	0.024	0.011	0.030	0.008	Mearns & Young, 1980
Alga (Enteromorpha)	Newport Bay	1980	5	0.002	0.003	0.001	0.004	0.001	MBC & SCCWRP,1980
Alga (Ulva)	Newport Bay	1980	5	0.160	0.154	0.032	0.306	0.108	MBC & SCCWRP,1980
Mysids (whole)	Palos Verdes	1980	8	0.032	0.032	0.017	0.054	0.011	Schafer et al.,1982
Zooplankton (whole)	Coastal	1980-81	5	0.002	0.002	0.001	0.005	0.002	Schafer et al.,1982
Black abalone	Palos Verdes	1976	5	0.022	0.027	0.004	0.037	0.015	Young et al., 1978
Black abalone	Santa Catalina Island	1976	3	0.024	0.022	0.006	0.043	0.019	Young et al., 1978
Gaper clams	Los Angeles Harbor	1979	5	0.020	0.015	0.010	0.042	0.013	Mearns & Young, 1980
Market squid	Coastal	1980-81	3	0.010	0.005	0.003	0.024	0.009	Schafer et al.,1982
Purple hinge scallop	Santa Catalina Island	1973/74	2	0.003	0.003	0.001	0.004	0.002	Young et al., 1978
Purple hinge scallop	Cortez Bank	1975	8	0.007	0.008	0.001	0.011	0.004	Young et al., 1978
Purple hinge scallop	Palos Verdes	1975/76	9	0.014	0.014	0.008	0.020	0.004	Young et al., 1978
Purple hinge scallop	Dana Point	1976	3	0.002	0.002	0.001	0.003	0.001	Young et al., 1978
Purple hinge scallop	Point Dume	1975-77	3	0.003	0.002	0.002	0.004	0.001	Young et al., 1978
California spiny lobster	Palos Verdes	1976	5	0.097	0.079	0.011	0.282	0.110	Young et al., 1978
California spiny lobster	Santa Catalina Island	1977	3	0.010	0.014	0.002	0.014	0.007	Young et al., 1978
Ridgeback prawn	Santa Catalina Island	1976	3	0.016	0.016	0.012	0.021	0.005	Young et al., 1978
Ridgeback prawn	Palos Verdes	1980	5	0.061	0.051	0.039	0.089	0.025	Schafer et al.,1982
Shore crab	Newport Bay	1980	5	0.004	0.003	0.002	0.007	0.002	MBC & SCCWRP,1980
Shore crab	Newport Bay	1980	3	All samples less than Detection level (.011)					MBC & SCCWRP,1980
Yellow crab	Dana Point	1976	3	0.032	0.038	0.020	0.039	0.011	Young et al., 1978
Spotted sand bass	Newport Bay	1978	3	0.242	0.198	0.064	0.465	0.204	Mearns & Young, 1980
Striped bass	Newport Bay	1978	3	0.246	0.295	0.120	0.324	0.110	MBC & SCCWRP,1980
Barred sand bass	Belmont Pier LA Harbor	1981	3	0.052	0.052	0.034	0.069	0.018	Gossett et al., 1983
Barred sand bass	Orange County	1981	5	0.021	0.021	0.015	0.030	0.006	Gossett et al., 1983
Striped mullet (adult)	Newport Bay	1978	3	0.821	0.718	0.425	1.320	0.456	Mearns & Young, 1980
Striped mullet (juvenile)	Newport Bay	1978	3	0.265	0.121	0.032	0.642	0.330	Mearns & Young, 1980
Striped mullet	Newport Bay	1980	10	0.089	0.050	0.008	0.268	0.095	MBC & SCCWRP,1980
Topsmelt	Newport Bay	1978	3	0.052	0.052	0.029	0.074	0.023	Mearns & Young, 1980
Topsmelt	Newport Bay	1980	10	0.032	0.027	0.002	0.089	0.033	MBC & SCCWRP,1980
White perch	Cabrillo Pier LA Harbor	1981	5	0.034	0.028	0.024	0.046	0.011	Gossett et al., 1983
White perch	Belmont Pier LA Harbor	1981	5	0.113	0.111	0.087	0.143	0.022	Gossett et al., 1983
Black perch	Cabrillo Pier LA Harbor	1981	5	0.029	0.024	0.019	0.051	0.013	Gossett et al., 1983
Black perch	Belmont Pier LA Harbor	1981	5	0.165	0.157	0.055	0.308	0.095	Gossett et al., 1983
California corbina	Belmont Pier LA Harbor	1981	4	0.149	0.045	0.009	0.494	0.232	Gossett et al., 1983
White croaker	Palos Verdes	1975	10	3.050	1.050	0.310	9.950	3.210	Young et al., 1978
White croaker	Los Angeles Harbor	1980	5	0.571	0.520	0.361	0.935	0.215	Mearns & Young, 1980
White croaker	Palos Verdes	1980	5	0.383	0.354	0.232	0.506	0.112	Schafer et al.,1982
White croaker	Belmont Pier LA Harbor	1981	5	0.101	0.093	0.055	0.175	0.051	Gossett et al., 1983
White croaker	Cabrillo Pier LA Harbor	1981	4	0.184	0.204	0.094	0.256	0.058	Gossett et al., 1983
White croaker	Dana Point	1981	7	0.047	0.024	0.012	0.173	0.057	Gossett et al., 1983
White croaker	Gerald Desmond Bridge	1981	5	0.418	0.414	0.155	0.642	0.206	Gossett et al., 1983
White croaker	Marina del Rey	1981	5	0.125	0.064	0.026	0.399	0.155	Gossett et al., 1983
White croaker	Navy, Long Beach Harbor	1981	7	0.141	0.086	0.046	0.386	0.119	Gossett et al., 1983
White croaker	Orange County	1981	10	0.017	0.016	0.008	0.027	0.007	Gossett et al., 1983
White croaker	Palos verdes	1981	2	0.876	0.876	0.176	1.575	-	Gossett et al., 1983

Table 15.5. (continued)

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	SOURCE
White croaker	Queen Mary Long Beach H	1981	6	0.122	0.089	0.034	0.311	0.103	Gossett et al., 1983
White croaker	Redondo area piers	1981	5	0.055	0.039	0.029	0.137	0.046	Gossett et al., 1983
White croaker	Santa Monica Bay	1981	5	0.203	0.225	0.069	0.334	0.095	Gossett et al., 1983
White croaker	Santa Monica Pier	1981	5	0.015	0.014	0.009	0.020	0.004	Gossett et al., 1983
White croaker	Santa Monica Bay	1981	5	0.099	0.079	0.039	0.224	0.076	Gossett et al., 1983
Mudsucker	Newport Bay	1979/80	3	0.040	0.048	0.008	0.049	0.020	MBC & SCCWRP,1980
Mudsucker	Newport Bay	1979/80	5	0.006	0.005	0.004	0.009	0.002	MBC & SCCWRP,1980
Yellowfin croaker	Newport Bay	1978	3	0.054	0.051	0.042	0.069	0.014	Mearns & Young, 1980
Yellowfin croaker	Newport Bay	1980	10	0.020	0.020	0.002	0.042	0.015	MBC & SCCWRP,1980
Queenfish (whole)	Cabrillo Pier LA Harbor	1981	5	0.058	0.050	0.030	0.095	0.029	Gossett et al., 1983
California halibut	Los Angeles Harbor	1980	4	0.154	0.150	0.127	0.190	0.027	Mearns & Young, 1980
California halibut	Newport Bay	1980	10	0.032	0.018	0.008	0.016	0.030	MBC & SCCWRP,1980
California halibut	Cabrillo Pier LA Harbor	1981	5	0.052	0.051	0.049	0.059	0.004	Gossett et al , 1983
California halibut	Belmont Pier LA Harbor	1981	4	0.062	0.059	0.023	0.107	0.034	Gossett et al , 1983
Flatfish	Belmont Pier LA Harbor	1981	5	0.021	0.017	0.010	0.039	0.011	Gossett et al , 1983
Dover sole	Gaviota	1977	5	0.020	0.010	0.001	0.048	0.022	SCCWRP, unpublished
Dover sole	Rincon	1977	6	0.074	0.071	0.046	0.127	0.032	SCCWRP, unpublished
Dover sole	Point Dume	1977	6	0.271	0.206	0.038	0.682	0.226	SCCWRP, unpublished
Dover sole	Santa Monica Bay	1977	2	0.233	0.180	0.126	0.273	0.076	SCCWRP, unpublished
Dover sole	Santa Monica Bay	1977	6	0.107	0.090	0.068	0.162	0.041	SCCWRP, unpublished
Dover sole	Santa Monica Bay	1977	5	0.166	0.085	0.070	0.498	0.186	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	3.166	1.735	0.681	10.423	.3.684	SCCWRP, unpublished
Dover sole	Huntington Beach	1977	4	0.870	0.832	0.493	1.324	0.354	SCCWRP, unpublished
Dover sole	Orange County	1977	6	0.174	0.173	0.100	0.246	0.058	SCCWRP, unpublished
Dover sole	Sunset Cliffs	1977	6	0.170	0.138	0.116	0.280	0.068	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	1.713	1.489	1.041	2.557	0.064	SCCWRP, unpublished
Dover sole	Palos Verdes	1980	5	0.278	0.255	0.162	0.505	0.133	Schafer et al ,1982
English sole	Rincon	1977	6	0.045	0.043	0.035	0.065	0.011	SCCWRP, unpublished
English sole	Santa Monica Bay	1977	4	0.905	0.840	0.769	1.172	0.181	SCCWRP, unpublished
Sablefish	Santa Monica Bay	1978	5	0.188	0.185	0.096	0.268	0.062	SCCWRP, unpublished
Pacific sanddab	Palos Verdes	1975	19	0.474	0.437	0.284	1.130	0.211	Young et al., 1978
Pacific sanddab	Dana Point	1975	10	0.026	0.023	<0.001	0.053	0.016	SCCWRP, unpublished
Pacific sanddab	Palos Verdes	1977	14	0.548	0.491	0.051	1.462	0.430	SCCWRP, unpublished
Pacific sanddab	Palos Verdes	1977	5	0.910	0.318	0.125	3.159	1.273	SCCWRP, unpublished
Pacific sanddab	Santa Monica Bay	1978	6	0.115	0.107	0.059	0.183	0.050	SCCWRP, unpublished
Pacific sardine	Coastal	1980-81	5	0.105	0.108	0.045	0.147	0.040	Schafer et al.,1982
Rockfish:									
Bocaccio	Santa Monica bay	1981	5	0.020	0.020	0.017	0.026	0.004	Gossett et al., 1983
Bocaccio	Palos Verdes	1980	7	0.149	0.107	0.078	0.382	0.106	SCCWRP, unpublished
Rockfish	Santa Monica Bay	1981	5	0.121	0.132	0.076	0.164	0.035	Gossett et al., 1983
Rockfish	Whites Point	1981	5	0.057	0.062	0.039	0.071	0.015	Gossett et al., 1983
Rockfish	Laguna Beach	1981	5	0.011	0.011	0.005	0.017	0.005	Gossett et al., 1983
Lizardfish	Santa Monica bay	1981	5	0.017	0.020	0.010	0.023	0.006	Gossett et al., 1983
Kelp bass	Whites Point	1981	5	0.0424	0.036	0.036	0.060	0.010	Gossett et al., 1983
California scorpionfish	Santa Catalina Island	1974-75	3	0.043	0.057	0.008	0.063	0.030	Young et al., 1978
California scorpionfish	Palos Verdes	1975	4	0.573	0.452	0.405	0.985	0.276	Young et al., 1978
California scorpionfish	Palos Verdes	1980	4	0.044	0.048	0.005	0.093	0.035	Schafer et al.,1982
California scorpionfish	Santa Monica Bay	1981	5	0.129	0.142	0.017	0.217	0.073	Gossett et al., 1983
California scorpionfish	Whites Point	1981	5	0.066	0.066	0.026	0.094	0.028	Gossett et al., 1983

Table 15.5. (continued)

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	SOURCE
Northern anchovy	Los Angeles Harbor	1980	5	0.065	0.063	0.036	0.102	0.024	Mearns & Young, 1980
Northern anchovy	Coastal	1980-81	5	0.008	0.005	0.003	0.024	0.009	Schafer et al.,1982
Pacific bonito	Coastal	1980/81	5	0.029	0.026	0.013	0.056	0.017	Schafer et al.,1982
Pacific bonito	Whites Point	1981	5	0.022	0.016	0.012	0.044	0.013	Gossett et al., 1983
Pacific bonito	Laguna Beach	1981	5	0.019	0.015	0.011	0.031	0.008	Gossett et al., 1983
Pacific hake	Coastal	1980-81	5	0.012	0.013	0.008	0.015	0.003	Schafer et al.,1982
Pacific mackerel	Santa Monica Bay	1981	5	0.015	0.018	0.007	0.023	0.007	Gossett et al., 1983
Pacific mackerel	Laguna Beach	1981	5	0.034	0.033	0.020	0.069	0.022	Gossett et al., 1983
Pacific mackerel	Coastal	1980-81	6	0.026	0.020	0.002	0.065	0.022	Schafer et al.,1982
Pacific mackerel	Whites Point	1981	1	0.012	-	-	-	-	Gossett et al., 1983
Jack mackeral	Coastal	1980/81	5	0.017	0.014	0.001	0.046	0.017	Schafer et al., 1982
Pacific barracuda	Whites Point	1981	5	0.047	0.042	0.037	0.060	0.011	Gossett et al., 1983
Swordfish	Coastal	1980-81	5	0.020	0.017	0.010	0.034	0.009	Schafer et al.,1982
Spiny dogfish	Palos Verdes	1980	5	5.120	3.100	0.400	14.800	5.744	Schafer et al.,1982
Spiny dogfish	Palos Verdes	1981	1	3.131	-	-	-	-	Gossett et al., 1983
Spiny dogfish	Whites Point	1981	3	7.380	5.584	1.742	14.815	6.719	Gossett et al., 1983
Thresher shark	Coastal	1980-81	5	0.015	0.015	0.006	0.021	0.006	Schafer et al.,1982
Mako shark	Coastal	1980-81	5	0.035	0.038	0.020	0.048	0.012	Schafer et al.,1982
White shark	Coastal	1980-81	3	0.041	0.039	0.037	0.047	0.005	Schafer et al.,1982
Basking shark	San Pedro	1981	1	0.004	-	-	-	-	Schafer et al.,1982
Blue shark	Coastal	1980/81	1	0.016	0.004	<.002	0.064	0.027	Schafer et al.,1982
LIVER									
Sablefish	Santa Monica Bay	1977	7	11.541	9.274	0.121	28.110	8.928	SCCWRP, unpublished
Dover sole	Gaviota	1977	5	1.084	0.598	0.001	4.019	1.545	SCCWRP, unpublished
Dover sole	Huntington Beach	1977	5	8.397	6.526	4.745	15.243	4.357	SCCWRP, unpublished
Dover sole	Orange County	1977	6	1.625	1.556	1.210	2.212	0.419	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	19.567	21.573	4.517	25.922	7.610	SCCWRP, unpublished
Dover sole	Point Loma, Sunset Cliff	1977	6	2.532	2.571	1.420	3.944	0.927	SCCWRP, unpublished
Dover sole	Rincon	1977	5	1.796	1.564	1.164	2.559	0.646	SCCWRP, unpublished
Dover sole	Santa Monica	1977	2	6.408	6.408	2.610	10.206	5.371	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	36.455	15.092	3.895	162.072	61.840	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	3	10.867	10.781	4.872	16.948	6.038	SCCWRP, unpublished
Dover sole	Gaviota	1985	2	0.392	0.392	0.385	0.398	0.010	Thompson et al., 1985
Dover sole	Laguna Beach	1985	1	0.423	0.423	-	-	-	Thompson et al., 1985
Dover sole	Tajiguas	1985	2	1.913	1.912	0.294	3.531	2.290	Thompson et al., 1985
English sole	Rincon	1977	6	0.412	0.430	0.216	0.537	0.107	SCCWRP, unpublished
English sole	Santa Monica	1977	6	14.397	15.073	5.009	22.340	7.520	SCCWRP, unpublished
Gulf sanddab	Port Hueneme	1985	1	4.772	4.772	-	-	-	Thompson et al., 1985
Gulf sanddab	Sorrento	1985	1	0.541	0.541	-	-	-	Thompson et al., 1985
Longfin sanddab	Carlsbad	1985	1	4.891	4.891	-	-	-	Thompson et al., 1985
Longfin sanddab	Imperial Beach	1985	1	12.174	12.174	-	-	-	Thompson et al., 1985
Longfin sanddab	La Jolla	1985	1	9.035	9.035	-	-	-	Thompson et al., 1985
Longfin sanddab	Laguna Beach	1985	1	5.739	5.739	-	-	-	Thompson et al., 1985
Longfin sanddab	San Clemente	1985	2	4.362	4.362	3.023	5.701	1.890	Thompson et al., 1985
Longfin sanddab	Sorrento	1985	1	9.322	9.322	-	-	-	Thompson et al., 1985
Pacific sanddab	Santa Monica Bay	1977	6	22.316	21.792	5.657	38.938	12.550	SCCWRP, unpublished
Pacific sanddab	Palos Verdes	1977	6	12.181	10.724	7.457	20.141	5.308	SCCWRP, unpublished

Table 15.5. (continued)

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	SOURCE
Pacific sanddab	Carlsbad	1985	1	2.957	2.957	-	-	-	Thompson et al., 1985
Pacific sanddab	Imperial Beach	1985	1	9.697	9.697	-	-	-	Thompson et al., 1985
Pacific sanddab	La Jolla	1985	1	1.580	1.580	-	-	-	Thompson et al., 1985
Pacific sanddab	Port Hueneme	1985	1	1.586	1.586	-	-	-	Thompson et al., 1985
Pacific sanddab	San Onofre	1985	2	7.620	7.620	5.182	10.058	3.450	Thompson et al., 1985
Pacific sanddab	Santa Barbara	1985	1	4.157	4.157	-	-	-	Thompson et al., 1985
Pacific sanddab	Trancas Canyon	1985	1	11.507	11.507	-	-	-	Thompson et al., 1985
Pacific sanddab	Ventura	1985	1	5.416	5.416	-	-	-	Thompson et al., 1985

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In an early survey, Valentine (1972) and Valentine and Soule (1973) reported concentrations of PCBs in 55 whole barred sand bass collected in four sampling regions in Baja California and southern California between 1969 and 1971. Average concentrations increased with latitude in 16 fish from southern Baja California to 5.534 ppm ww in 26 fish from San Clemente. The large-scale geographic gradient was similar to that for DDT. However, the authors expressed concern about the absolute concentrations. Reanalysis in 1972 of extracts of six fish from San Clemente by CSDLAC (unpublished data) produced a mean tPCB concentration of 0.597 ppm ww, which is lower by a factor of 9.3 than the mean value of all 26 fish initially analyzed by Valentine (1972).

Within the data presented in Table 15.5 are several regional comparisons. The most regionally extensive were surveys of Dover sole or other flatfish collected in 1971 (SCCWRP, 1973), 1974 (McDermott et al., 1975), 1977 (Young, Mearns, and Gossett, 1991), and 1985 (Thompson et al., 1987). Data for all Dover sole sampled by SCCWRP, 1971-80, are summarized in Table 15.5 and in Figures 15.15 and 15.16. As shown in Figure 15.15, mean tPCB concentrations in muscle of Dover sole collected in 14 areas in 1971-72 ranged nearly 60-fold from 0.04 ppm ww at Santa Catalina Island to 2.36 ppm ww at Palos Verdes. High concentrations were also found in fish from Santa Monica Bay and there appeared to be a tendency for concentrations to fall off markedly west of Santa Monica Bay (0.08 to 0.12 ppm ww) but to remain somewhat elevated across San Pedro Bay (0.2 to 0.71 ppm ww; Figure 15.16). An important change was evident in the 1973-74 survey (Figure 15.16); concentrations appear to rise dramatically in fish from San Pedro Bay and from Dana Point. The only known major management action at this time that could have led to increased PCB contamination of San Pedro Bay flatfish was initiation of deep water sewage discharges by the Sanitation Districts of Orange County.

Another regionally extensive collection was of Dover sole and other flatfish taken in 1977 between Gaviota and San Diego (Sunset Cliffs) by SCCWRP as part of the 60-m survey (unpublished data, SCCWRP). Mean muscle PCB concentrations in bottom fish along the shelf ranged from 0.01 ppm ww at Dana Point to 3.17 ppm ww at Palos Verdes. Concentrations were moderate (0.1 to 0.8 ppm ww) in Dover sole from urban coastal shelf regions such as Santa Monica Bay (Point Dume to Redondo), off Huntington Beach, and San Diego. The gradient suggests concentrations increased about 20-fold between Gaviota and Point Dume and another 15-fold between Point Dume and Palos Verdes, decreasing again to the south of Palos Verdes.

However, in 1981 white croaker from popular shore fishing areas in Los Angeles-Long Beach harbors, and from deep water sites in Santa Monica Bay contained PCB concentrations nearly exceeding those at Palos Verdes (Gossett et al., 1982; 1983a). For example, highest PCB concentrations in white croaker during 1980-81 were in Los Angeles Harbor near the Gerald Desmond Bridge (0.418 ppm ww) and at the sludge outfall 7 miles offshore in Santa Monica Bay (0.203 ppm ww). By comparison, Palos Verdes produced white croaker with 0.383 ppm ww in 1980 and 0.876 ppm ww in 1981. The PCB concentrations found during this 1981 sportfish survey were largely responsible for the posting of seafood consumption advisories along much of the Los Angeles County coastline.

There is evidence that prior to the mid-1980s, some other bays and harbors may have contained fish with PCB concentrations comparable to those at Palos Verdes. For example, in 1978 spotted sand bass, striped bass, and striped mullet from Upper Newport Bay contained mean PCB concentrations of 0.242, 0.246, and 0.821 ppm ww, respectively (Table 15.5).

Tissue contaminant results are available for a large number of fish species in the Southern California Bight (see Table 15.5); but the bass species (for example, kelp bass and barred sand bass) have been studied with the most frequency across studies and are species of economic importance, especially in the southern California recreational fishery. For these reasons, the bass were selected as focal points for the further discussion of recent geographic trends of PCBs in fish muscle.

Three data sets were analyzed extensively for this report. The LARWQCB, which oversees water quality-related activities in the ocean around Los Angeles, contracted a study conducted in 1985 (Risebrough, 1987) that sampled and analyzed both muscle and liver of kelp bass from 15 sites along the coast of the Palos Verdes Peninsula and near Point Dume, as well as sites in offshore islands. The CSDLAC have monitored kelp bass (muscle only) around Palos Verdes for nearly 20 years as a condition of their NPDES permits. The Benthic Surveillance Project of NOAA's NS&T Program has examined sediments and associated barred sand bass (liver only) at six sites from Santa Monica to San Diego.
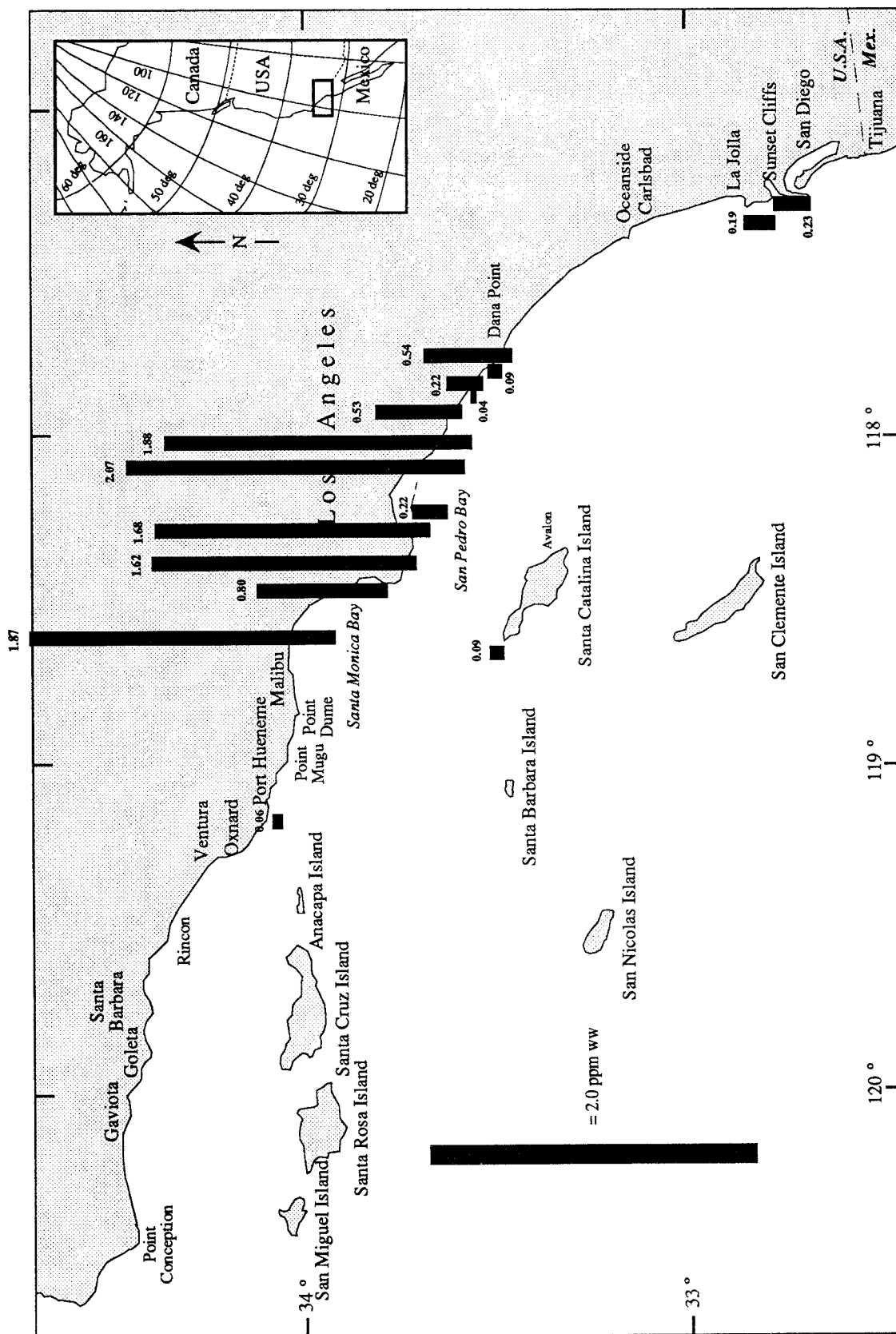
Figure 15.16. tPCB in muscle of Dover sole 1971-72. Source: McDermott et al., 1975.
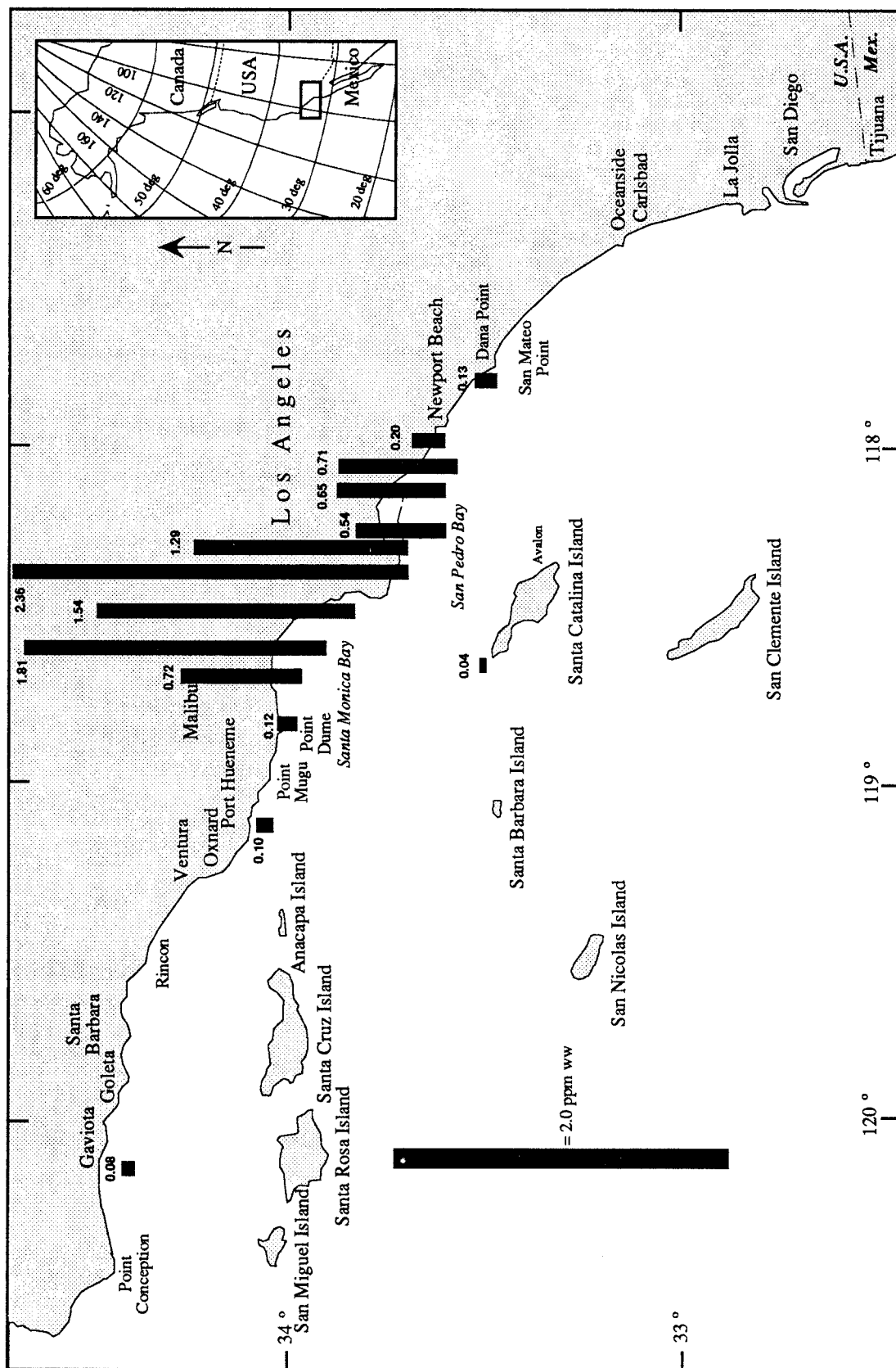
Figure 15.16. tPCB in muscle of Dover sole1973-74. Source: McDermott et al., 1975.

PCBs were measured in muscle of kelp bass from 10 sites in 1985 by LARWQCB and CSDLAC (Figure 15.17). These measurements are consistent with results of sediment and mussel surveys in that elevated PCB concentrations were shown to occur around the Palos Verdes peninsula. Nowhere within the survey area did concentrations approach the FDA action limit of 2.00 ppm ww. Average site values ranged from 0.01 ppm ww at Santa Barbara Island to 0.20 ppm ww at Point Fermin (Figure 15.17).

Liver tissue has been less frequently sampled than muscle in fish of the Bight. Mean concentrations in nearly a dozen species have ranged from 0.392 ppm ww in 1977 Dover sole from Gaviota to 36.445 ppm ww in 1977 Dover sole from Palos Verdes (Table 15.5).

A coastal reference survey that included analyses of sanddab was conducted in 1985 by SCCWRP (Thompson et al., 1987). Concentrations of tPCBs in sanddab liver ranged from 2 to 15 ppm ww. This survey identified an intriguing gradient of increasing liver PCB concentrations approaching the United States-Mexico international boundary; concentrations in sanddab liver increased about twofold from 3 to 6 ppm ww in the Dana Point area, to over 10 ppm ww off San Diego and near the United States-Mexico boundary. This is in partial agreement with results of the 1986 NOAA NS&T Mussel Watch results (Figure 15.9)

Total PCBs were measured in livers of kelp bass and sand bass at 13 sites in 1984 and 1985 by LARWQCB, SCCWRP, and the NOAA NS&T Program's Benthic Surveillance Project (Figure 15.18). Site mean and composite values ranged from 0.16 ppm from kelp bass captured at East End, Santa Catalina Island, to 6.84 ppm in barred sand bass from two San Diego Harbor composites.

Of the 13 sites surveyed, San Diego Harbor clearly yielded the most contaminated bass livers. This agrees with a number of sediment surveys and with CMW results that had previously indicated a potential problem with elevated levels of PCBs in the harbor. Comparison of these two species (barred sand bass and kelp bass) appears to be reasonable because levels in barred sand bass from Dana Point (0.58 ppm ww in 1984, and 0.63 ppm in 1985) were comparable to the average concentration in 1985 collections of liver of kelp bass collected from nearby San Mateo Point (0.40 ppm ww; Figure 15.18).

Data on concentrations of PCBs in liver of three species of fish from the 1984 and 1985 NOAA NS&T Benthic Surveillance surveys are in partial agreement with the trends and patterns described above from regional and local surveys. Concentrations were higher in fish (hornyhead turbot, barred sand bass, and white croaker) from three Los Angeles-area inshore urban sites (Seal Beach, San Pedro Canyon, and Santa Monica Bay) and in San Diego Harbor (barred sand bass) than at the Dana Point reference site (white croaker; Figures 15.19 and 15.20). However, although the 1985 SCCWRP reference survey (Thompson et al., 1987) identified high PCB concentrations in sanddabs from the outer coast off San Diego, the NS&T hornyhead turbot samples did not reveal correspondingly high concentrations outside San Diego Harbor (San Diego Bay)

In summary, fish of the coastal zone of the Bight have demonstrated strong but species-specific regions of PCB contamination gradients, with an overall average in muscle tissue about 0.2 to 0.4 ppm ww for nearshore fish at 0.02 to 0.04 for pelagic species. It appears that in 1985 there were at least two epicenters of PCB contamination of bass in the Southern California Bight: near the Palos Verdes Peninsula and in San Diego Harbor. Concentrations in muscle and liver tissue were about an order of magnitude lower in fish from three offshore islands and from the southern Orange County coast in 1984 and 1985 compared to the Palos Verdes Peninsula.

Some authors have interpreted fish body burden results in the context of exceedances of U.S. FDA guidelines. Smokler et al. (1979) evaluated DDT concentrations obtained in the CSDLAC study in this manner. Although they did not provide such an analysis for PCBs, reported data may be summarized in this way. Between 1971 and 1975, the percent of fish exceeding FDA guidelines for PCB (2.0 ppm ww) ranged from 0 to 12 percent each year. From 1976 to 1985, no PCB concentrations exceeded the guidelines. In interpreting these results, it should be borne in mind that tPCB was defined for the CSDLAC data set as the sum of Aroclors 1254 and 1242. Although these are usually the most abundant Aroclor mixtures, defining tPCB in this fashion underestimates the true total since other PCB compounds may also have been present. In addition, it is clear that spiny dogfish from Palos Verdes have greatly exceeded the FDA action limit. Since this species has not been sampled from other sites, it is not clear that these very high concentrations are restricted only to the Palos Verdes Peninsula.
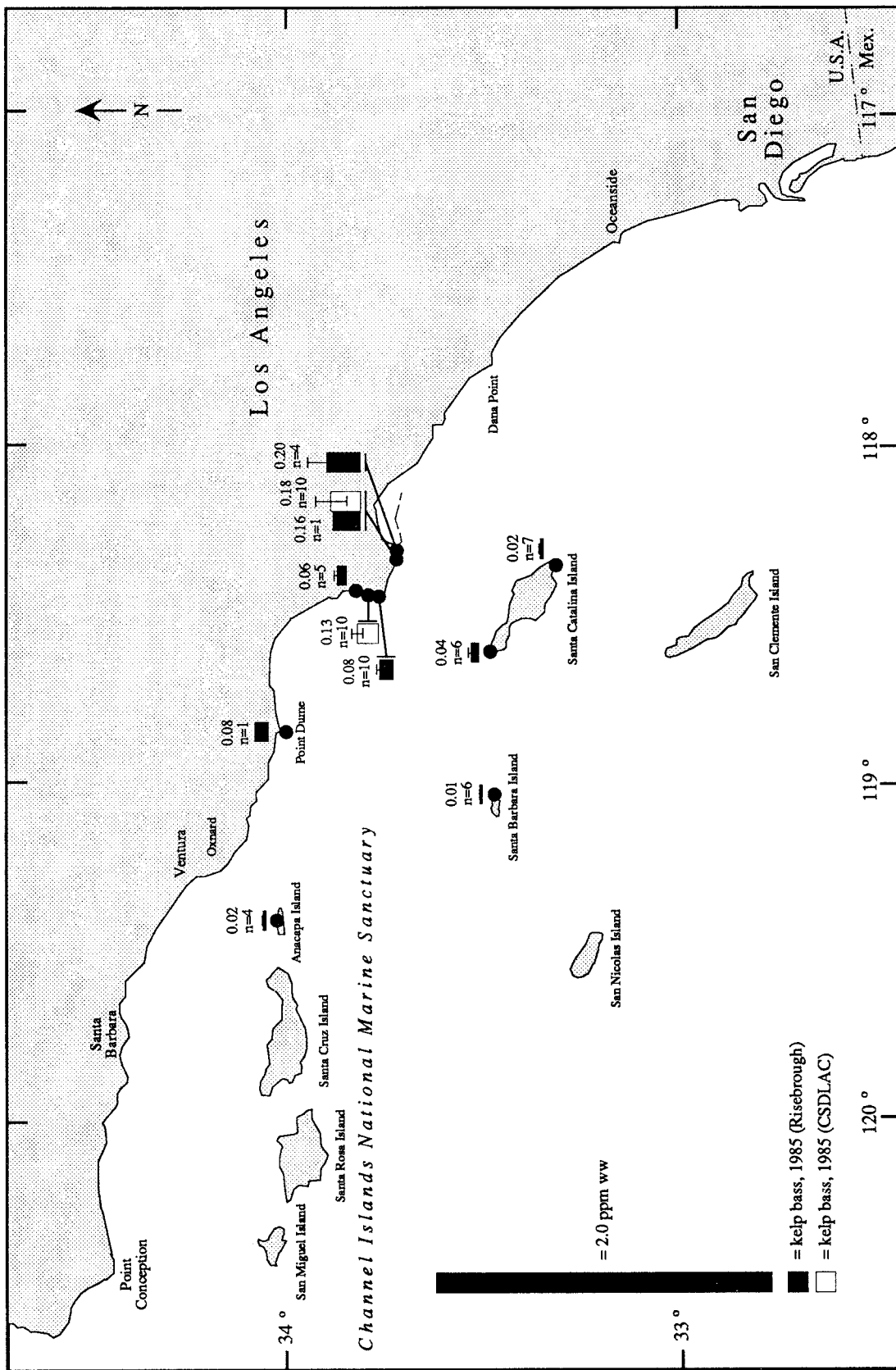
Figure 15.17. Wet weight concentrations of tPCB measured in muscle tissue of kelp bass sampled in the Southern California Bight in 1985. Sources: Risebrough (1987); CSDLAC (unpublished).
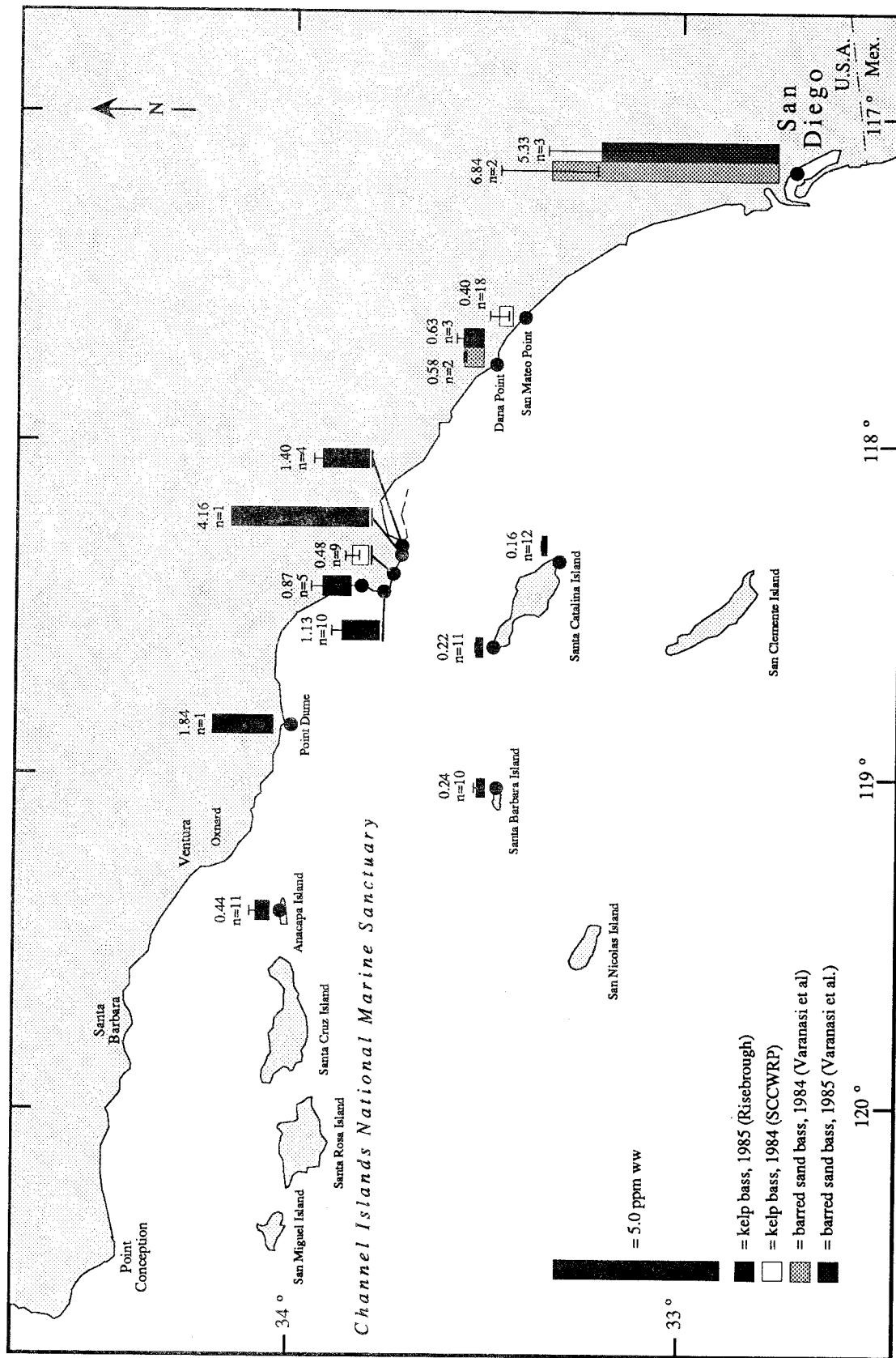
Figure 15.18. Wet weight concentrations of tPCB measured in liver tissue of bass species sampled in the Southern California Bight in 1984 and 1985.
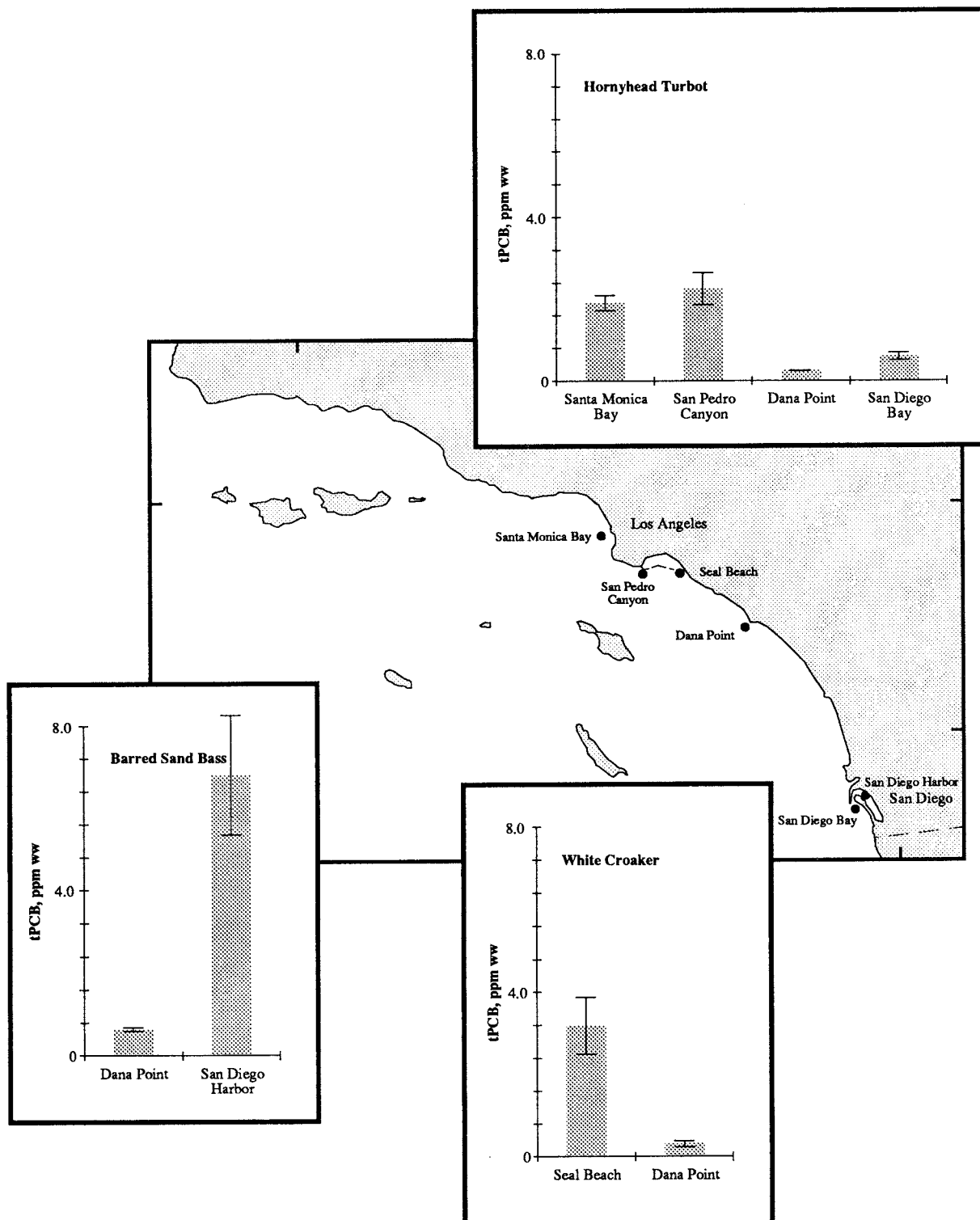Sources: Risebrough, 1987; SCCWRP, unpublished; and Varanasi et al., 1988.

Figure 15.19. Concentrations of tPCB measured in liver tissue of three fish species collected in the Southern California Bight in 1984, Source: Varanasi *et al.*, 1988.
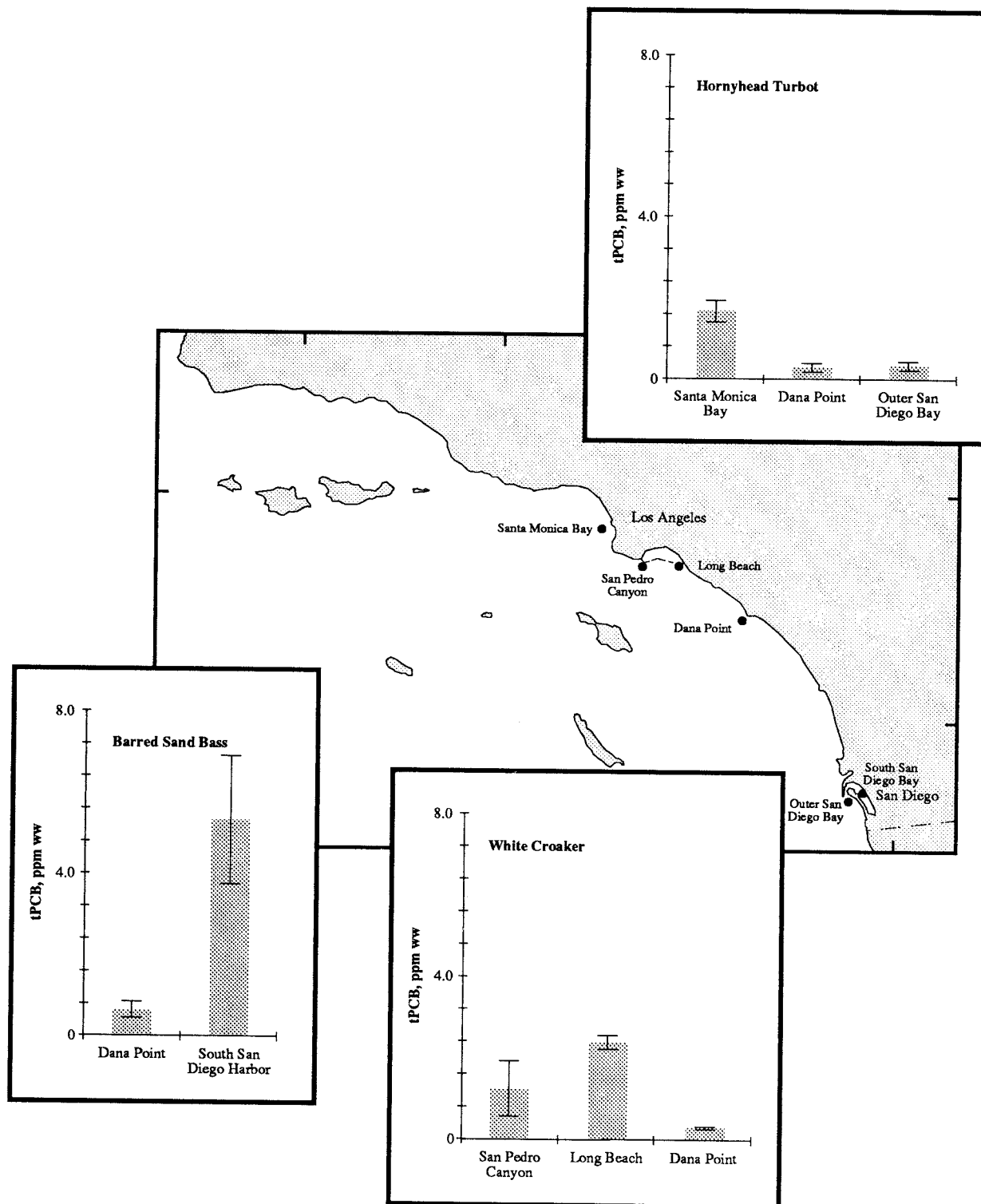
Figure 15.20. Concentrations of tPCB measured in liver tissue of three fish species collected in the Southern California Bight in 1985. Source: Varanasi *et al.*, 1988.

The U.S. FDA action limit (2.0 ppm ww) is among the lowest action limits internationally for PCBs in fish, shellfish, or their products (range 1 to 5 ppm ww; Nauen, 1983). Interestingly, two nations, Sweden and The Netherlands, also have PCB limits that apply to fish liver (5 and 25 ppm ww, respectively). If applied to the data reported here (Table 15.5), livers of many sanddabs collected in 1985 between Santa Barbara and Port Hueneme, off Trancas Canyon in northern Santa Monica Bay, at Laguna Beach, and along the coast between Carlsbad and Imperial Beach would exceed the Swedish standard of 5 ppm ww, as would Dover sole from Palos Verdes and barred sandbass from San Diego Harbor.

Temporal Trends

The bulk of the data suggest that concentrations in fish muscle on a regionwide basis are lower now than in the 1970s. The "average" fish collection of the data-rich 1976-77 period contained about 0.4 ppm ww of PCB (overall mean of 32 1976-77 collection means; range 0.010 to 3.17 ppm ww); whereas, the "average" fish collection of the comparably data-rich 1980-81 period contained about 0.2 ppm ww of PCB (overall mean of 5.0 1980-81 collection means; range 0.11 to 5.12 ppm ww). Although, this is inadequate evidence to claim a decrease of a factor of 2 in 4 to 6 years, it does not indicate increasing contamination. Furthermore, substantial evidence exists for an even greater decrease for specific species in urban areas.

MacGregor (1974) analyzed whole body tissue concentrations of Aroclor 1254 in preserved specimens of the *S. leucopsarus*, in an attempt to elicit long-term (1940 to 1972) trends in contamination. Values obtained ranged from below detection and quantitation limits (probably about 0.01 ppm ww) in many fish, to 9.94 ppm ww in a fish collected in Santa Monica Bay in 1955. However, unlike results for DDT (chapter 16), no discernible pattern for the PCB mixture was determined (either geographically or temporally). MacGregor noted that although a relatively greater percentage of the fish sampled near Los Angeles and the Palos Verdes Peninsula had higher concentrations of Aroclor 1254, fish collected 175 to 200 nautical miles offshore contained PCBs at elevated levels as well. Analysis of temporal results from the same sites showed a similar lack of a discernible trend.

Monitoring efforts by CSDLAC offer the longest continuous time series of direct fish body burden measurements available for the Southern California Bight. NOAA's Benthic Surveillance Project samples annually but has been in existence only since 1984. Other studies, such as LARWQCB's 1985 study, have represented one-time synoptic sampling programs. Large-scale reductions in tissue levels might have occurred in the years preceding 1984 because inputs of chlorinated organic compounds such as PCBs were substantially reduced in the 1970s.

For kelp bass, an analysis of CSDLAC data from 1971 to 1988 demonstrates a trend of decreasing muscle tissue concentrations of PCBs (figure 15.21). The results from CSDLAC analyses were grouped by location type (offshore island or mainland) and the nonparametric Mann-Whitney test (Zar, 1984) was employed to test the null hypothesis that there was no difference between the island and mainland results. At $\alpha = 0.01$, a significant difference was determined and the mainland and island data sets were analyzed separately.

A nonparametric correlation statistic, Spearman's rank procedure (Zar, 1984), was used to evaluate the correlation of tPCB with time. In the case of the mainland sites, the correlation for tPCB in relation to time was significant ($\alpha = 0.01$) and negative: $r_s = -0.647$ at a significance level less than 0.001. At the island sites, the r_s was -0.290 at a significance level of 0.202. Therefore, with $\alpha = 0.01$, the relationship between declining PCB concentrations with time was significant only at the mainland sites.

Analysis of the length of fish sampled over the course of the CSDLAC monitoring showed that larger fish were selected in later years. To minimize body burden impacts associated with size a second correlation analysis was performed on island and mainland fish that fell within the range of 29 to 32 cm. This range was common to both earlier and later years of sampling. Restricting the data sets in this fashion resulted in a stronger correlation at mainland sites of $r_s = -0.750$ for tPCB at a significance level less than 0.001; the resulting sample size for island sites was too limited for meaningful analysis.
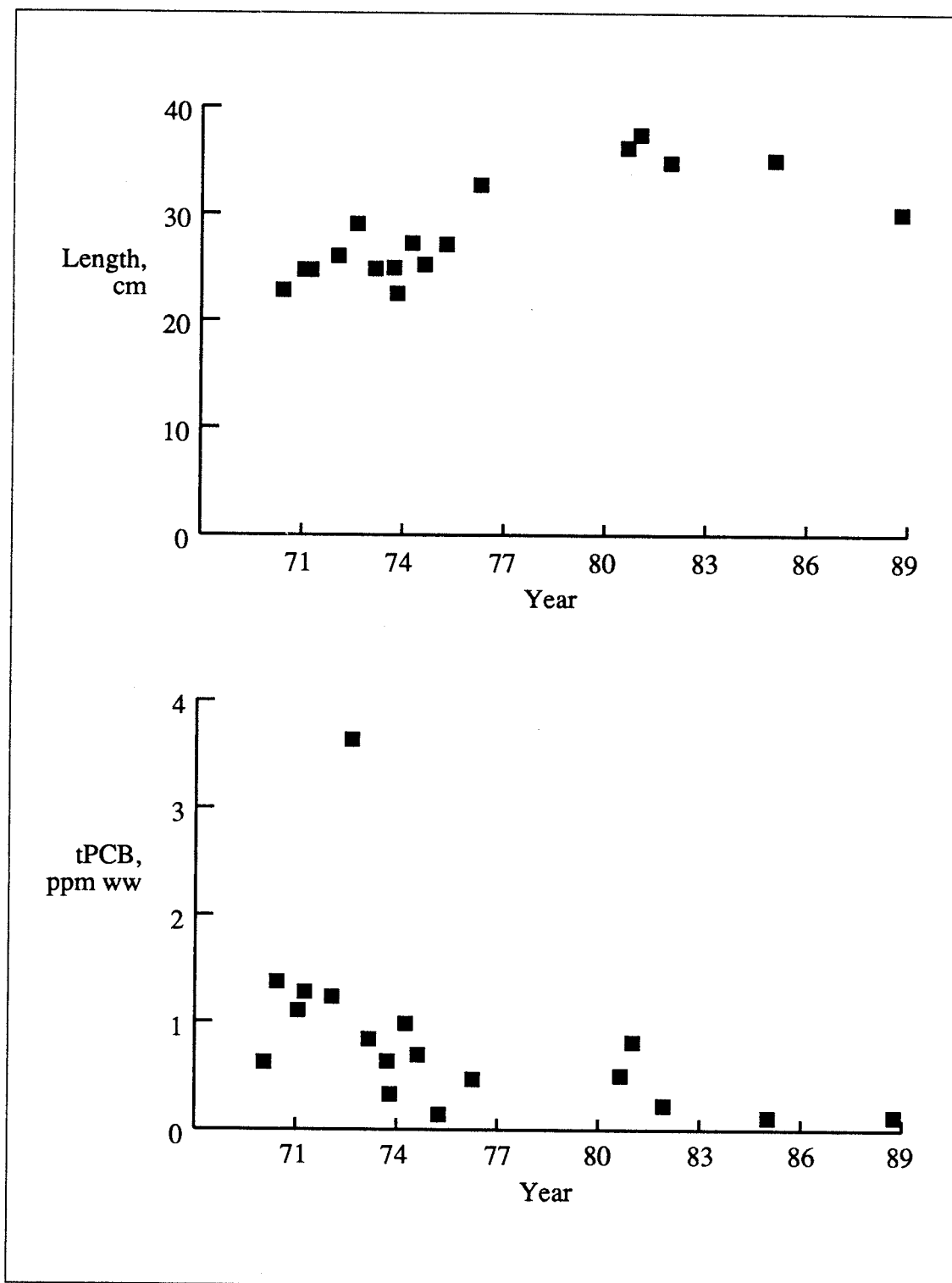
Figure 15.21. Time series of tPCB in muscle and length of kelp bass from Palos Verdes 1971-88. Source: CSDLAC unpublished data.

Results of analyses of Dover sole muscle can also provide information on trends in PCBs near the CSDLAC outfalls at Palos Verdes. CSDLAC has monitored Dover sole since 1971 in southern Santa Monica Bay and around the Palos Verdes outfalls (figure 15.22). SCCWRP also analyzed muscle tissue of Dover sole from the Palos Verdes outfall areas during the same time period (Young, Gossett, and Heesen, 1988). Concentrations of tPCBs were highly variable during the early 1970s and appear to have declined in more recent years. There is limited information to estimate trends over time of PCBs in muscle of white croaker (figure 15.23). CSDLAC and SCCWRP (Young et al., 1978, Schafer et al, 1982, and Gossett et al., 1983b) have sampled white croaker from the Palos Verdes Peninsula since 1971. Concentrations of tPCBs in white croaker muscle also appear to have declined between 1971 and 1988.
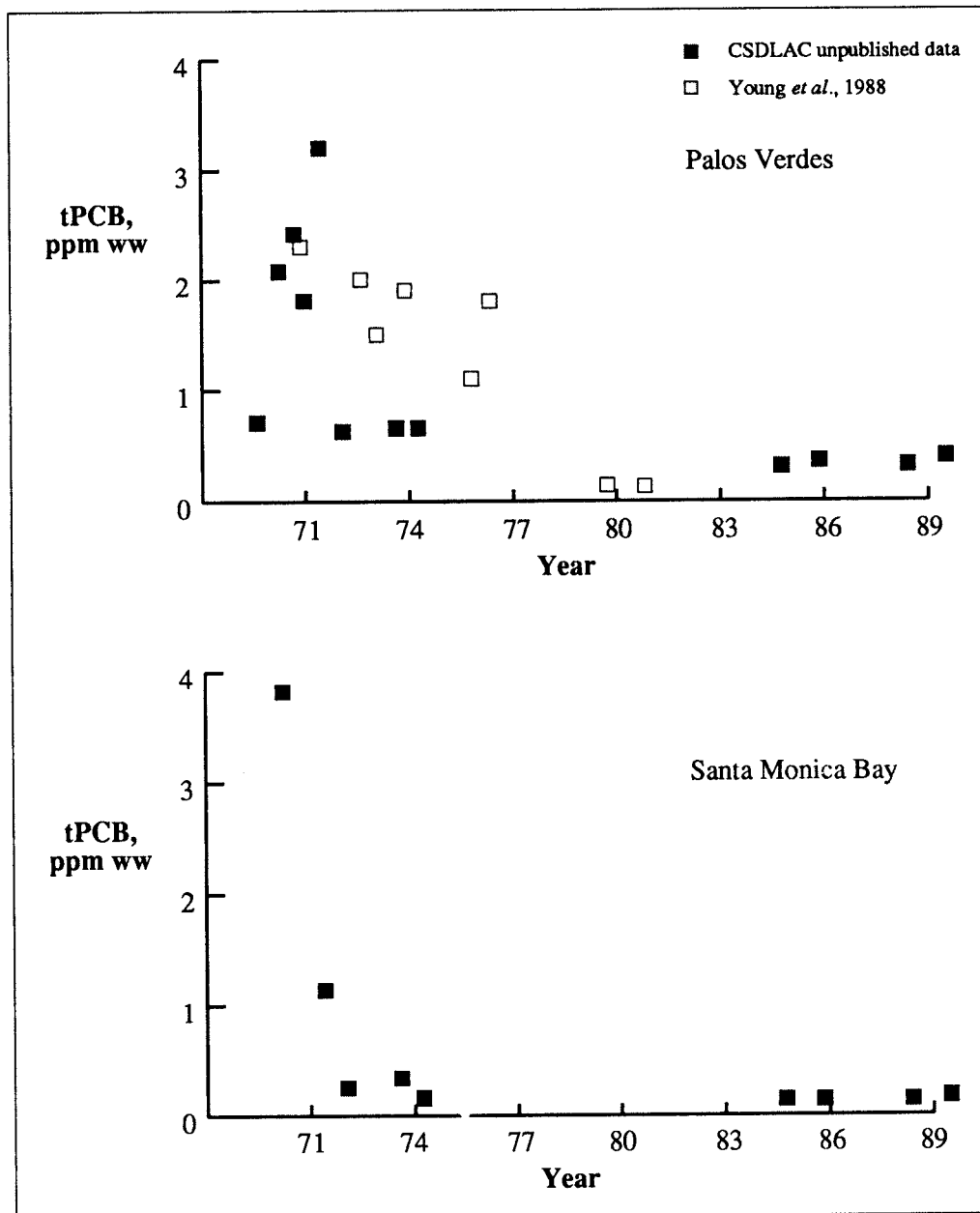
Figure 15.22. Time series of tPCB in muscle of Dover sole sampled at Palos VErdes and Santa Monica Bay 1971-89. Sources: Young et al., 1988; CSDLAC, unpublished data.
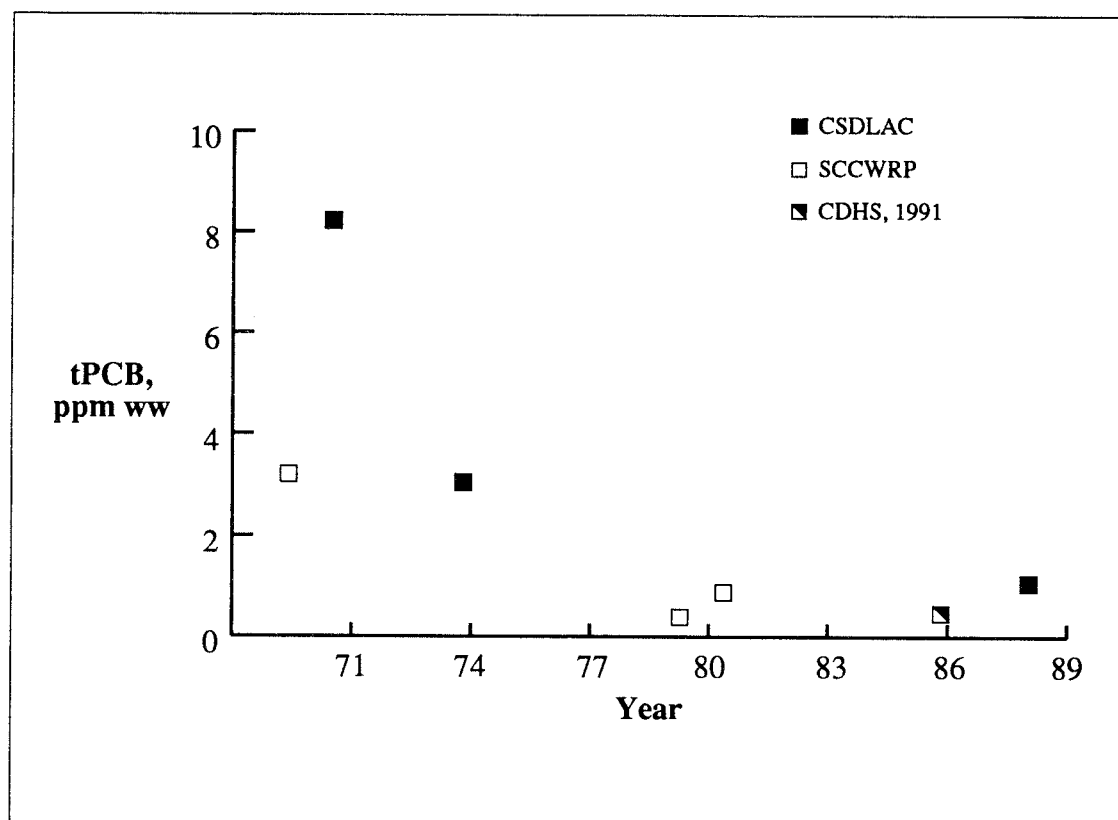
Figure 15.23. Time series of tPCB in muscle of white croaker from Palos Verdes 1971-88. Sources: CSDLAC, unpublished data; SCCWRP, unpublished data: CDHS, 1991.

SUMMARY AND CONCLUSIONS

Despite analytical and interpretive difficulties inherent to the evaluation of environmental PCB contamination, measurements of PCB concentrations in sediments, mussel tissue, and fish tissue in the Southern California Bight have indicated three regions of elevated levels: San Diego Harbor, the coastal shelf along the Palos Verdes Peninsula, and Los Angeles-Long Beach harbors. Portions of San Diego Harbor have yielded consistently high concentrations of PCBs measured in sediment, mussels, and fish, with some concentrations very high relative to other southern California, West Coast, and national measurements. A source of PCBs in San Diego Harbor has been identified, and remedial actions are underway. In the case of the Palos Verdes shelf, the JWPCP outfall located offshore and estimated to have discharged thousands of kg of PCBs over the past 20 years, is an obvious explanation for the elevated concentrations encountered in that region. Sources for the high levels measured in the Los Angeles-Long Beach harbors region, however, are not as easily pinpointed, and may represent previously unidentified industrial sources or diffuse nonpoint sources.

Although PCBs are known to be resistant to degradation in the environment, major new inputs in the Southern California Bight have been curtailed and data indicate that environmental levels are in fact declining. Recent moderately high concentrations found in some seafood organisms off southern California have resulted in consumption advisories being posted by health officials, but concentrations in edible tissues exceeding FDA limits of 2.0 ppm ww appear to be rare and could reasonably be expected to remain so.

INFORMATION NEEDS

Since the concentration of PCBs in sewage effluents from southern California treatment plants has fallen below a detection limit of 0.05 ppb, mass emission rates of PCBs from outfalls can no longer be calculated. If detection limits for wastewater analyses were lowered, further trends in emission rates for PCBs could be evaluated. It would also be useful to reassess atmospheric deposition and runoff of PCBs to the Southern California Bight.

The apparent declines in concentrations of PCBs in sediment should be verified with further analyses of sediment from the Palos Verdes peninsula and other areas. Since concentrations of PCBs in sediment from several areas fall within a range that is likely to cause adverse biological effects, further evaluation of the toxicity of sediment from Los Angeles-Long Beach and San Diego harbors should be performed. Analyses of PCBs in sediment, shellfish, and fish should move toward methods that evaluate concentrations of individual PCB congeners. This would reduce error and permit evaluations of concentrations of the most toxic compounds, and may help identify sources.

Many researchers have noted that variability in concentrations of PCBs is reduced when values are normalized to TOC (in sediments) or lipid content (in fish and shellfish). Young, Mearns, and Gossett (1991) have demonstrated that by normalizing sediment Aroclor 1254 to TOC and normalizing Dover sole muscle to its lipid content, the ratio of concentrations in sediment to that in fish muscle from the same area is reduced to approximately 1:1. This relationship appears to hold over a wide range of concentrations although was tested with only a small number of samples. It would be useful to test this model with more samples and other benthic species. This model could be useful in predicting levels of contamination in bottom fish when concentrations of PCBs in sediment are known.

Apparent declines in concentrations of tPCBs in fish muscle (especially white croaker) should be verified with further analyses from the Palos Verdes peninsula, Los Angeles Harbor, and Santa Monica Bay.

CHAPTER 16
DICHLORODIPHENYLTRICHLOROETHANE

Dichlorodiphenyltrichloroethane (DDT) is probably the most familiar of the organochlorine pesticides. Discovered in 1874, the DDT family of compounds (including degradation products such as dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD)) was not identified as a potent insecticide until 1940. The acute toxic effect of DDT and its resistance to degradation made it particularly effective in this capacity. During World War II, DDT saw widespread use as a delousing and mosquito control agent. Manufacture and use grew tremendously following the war, and DDT was used to control a broad spectrum of agricultural, silvicultural, and household insect pests. Total DDT consists of the sum of six individual isomers: p,p' DDE; o,p'DDE; p,p'DDD; o,p'DDD; p,p'DDT; and o,p'DDT.

Possible detrimental environmental impacts of indiscriminate application of DDT were noted as early as the 1940s (Linduska, 1949; DeWitt et al., 1955), but it was the 1961 publication of Rachel Carson's popular book, Silent Spring, that focused attention on the serious nature of those impacts. The book documented population declines and reproductive failures in birds exposed to DDT residues intended to control insect pests. Subsequent studies verified that DDT disrupted calcium metabolism in birds, which resulted in eggshell thinning and reduced reproductive success. However, these and other effects have been disputed (Claus and Bolander, 1977). DDT is moderately toxic to humans. It is also an animal carcinogen and is considered by the EPA to be a potential human carcinogen. DDT appears to be considerably less carcinogenic than PCBs. The U.S. EPA suspended manufacture for general application of DDT in the United States in 1972.

There is evidence to indicate that organic contaminants (especially PAHs) are converted to oxygenated metabolite compounds in the water column, sediments, and fish. Brown et al. (1987) measured parent DDT compounds and oxygenated metabolites of DDT in sediment, shrimp (Sicyonia ingentis), M. californianus, and scorpionfish using gas chromotography/electron capture detection GC/ECD and GC/MS instrumentation. They reported that oxygenated metabolites usually represented the majority of total DDT (tDDT) compounds (48-99%). However, Gossett (1988) found that these results were not reproducible using different GC/MS instruments. GC/MS instruments did not detect any oxygenated metabolites measured using GC/ECD instruments. This discrepancy could be caused by detection limit problems or by incorrect ECD assignments. The results of Brown et al. (1987) may therefore be questionable.

Inputs of DDT to the Bight have been the subject of considerable research, monitoring, and debate. For the year 1971, SCCWRP estimated that total non-advective inputs were 45 mt, distributed as follows: wastewater discharge, 42 percent (19 mt); ocean dumping, 31 percent (14 mt); rainfall, 4.4 percent (2 mt); and surface run-off, 0.2 percent (0.1 mt). At that time, the largest single input was the JWPCP outfall discharging at Whites Point on the Palos Verdes peninsula. This plant received wastes from Montrose Chemical Corporation in Torrance. Inputs from the treatment plant were independently estimated at 21,700 kg (21.7 mt) in 1971 but decreased to 73 kg (0.073 mt) by 1985 (SCCWRP, 1987a). By comparison, DDT emissions from the Los Angeles River were 630 kg in 1971 and 1972, 270 kg in 1979 and 1980, and 20 kg in 1985 and 1986. Thus, sewage emissions of this pesticide are now within a factor of 4 or less than riverine and nonpoint source inputs. DDT and other chlorinated hydrocarbons evaporate along with water from damp soil and are associated with dust and other particulate matter in air. Wind then distributes these materials widely. This would account for the broad distribution of DDT in oceanic sediments.

The presence of elevated levels of DDT in sediments and marine biota of the Southern California Bight is well documented. The major source for this contamination was identified through monitoring by the CSDLAC at the Montrose Chemical Company, which manufactured DDT from 1947 to 1982 (Hayes and Phillips, 1987) and produced two thirds of the DDT sold worldwide in 1970 (MacGregor, 1974). Although use of DDT in the United States peaked in 1959, a substantial portion of the company's production was exported. Monitoring of Montrose Company discharges in 1970 indicated that approximately 640 pounds of DDT compounds were entering the Los Angeles County waste system daily (Carry and Redner, 1970).

Montrose discharged DDT manufacturing wastes into the CSDLAC treatment system until 1970, after that the wastes were hauled to landfills and storage facilities until production was terminated in 1982 (Chartrand, 1988). During the 1950s, the manufacturer also dumped DDT wastes into the coastal waters of the San Pedro Channel between Los Angeles and Santa Catalina Island (Risebrough, 1987). Run-off from

the Torrance plant site apparently entered Los Angeles-Long Beach harbors and resulted in DDT contamination of that localized area as well. In 1983, the LARWQCB and the U.S. EPA issued Cleanup and Abatement Orders to Montrose (Hayes, *et al.*, 1985). In response to this action, the company commenced plant site cleanup and DDT source control measures.

Discharge records documenting mass emissions of DDT from the seven major municipal wastewater treatment plants in the Southern California Bight illustrate the effectiveness of control actions employed since the early 1970s (Figure 16.1). The annual level of DDT discharge by municipal plants declined by a factor exceeding 350 from 1971 to 1985 (SCCWRP, 1987a).
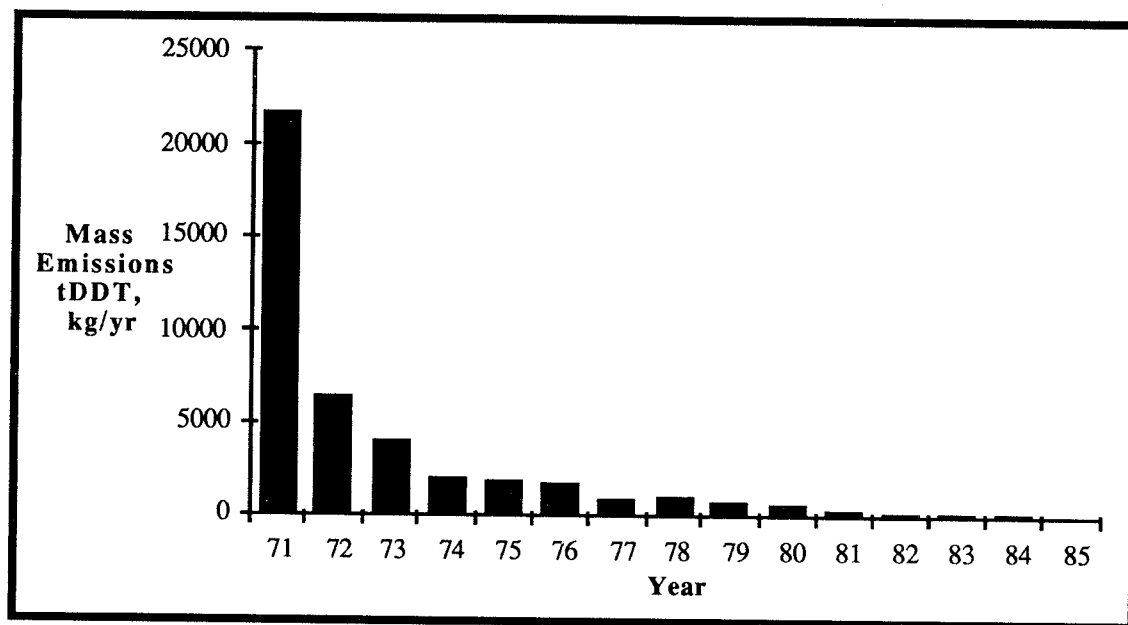
Figure 16.1. Combined annual mass emissions of total DDT for seven southern California municipal wastewater dischargers, 1971-85. Source: SCCWRP, 1987.

DDT IN SEDIMENT

Thousands of samples of sediments from the Southern California Bight have been measured for DDT contamination. Most of the data are from discharger monitoring programs at Palos Verdes, in Santa Monica Bay, near the Orange County outfall area off Huntington Beach, and at Point Loma.

Synoptic (regionwide) sediment surveys include a 1971-72 survey at five major discharge sites (SCCWRP, 1973), a 1971 survey across the San Pedro shelf (MacGregor, 1976), the 1977 SCCWRP 60-m survey (Word and Mearns, 1979), the 1984-86 NOAA NS&T Benthic Surveillance and Mussel Watch surveys, and a 1985 SCCWRP Reference Survey (Thompson *et al.*, 1987).

Total DDT concentrations in sediments from selected surveys have ranged over 5 orders of magnitude (100,000-fold) from 0.001 ppm dw at sites off Point Loma in 1977 to 175 ppm dw at a 60-m deep site sampled in the same year along the Palos Verdes shelf near Whites Point (Table 16.1). In addition to Palos Verdes, the most heavily contaminated sites have included the Los Angeles-Long Beach harbors area (mean concentration 0.51 ppm dw in 1973 and 0.10 ppm dw in 1978) and Upper Newport Bay (mean 0.18 ppm dw in 1980; Table 16.1). Feldmeth (1980) cites concentrations ranging from 3.19 to 7.18 ppm dw in sediments in 1979 and 1980 from Bolsa Bay, a lagoon area that receives run-off from the East Garden Grove-Wintersburg flood control channel in Huntington Beach and that, in turn, drains into Huntington Harbor and Anaheim Bay.

Table 16.1. Mean, median, minimum, and maximum tDDT concentrations in surface sediment from selected surveys, 1970-85 in ppm dw.

SITE	YEAR	N	Mean	Median	Minimum	Maximum	Standard Deviation	Source
Rural Coastal Shelf (60 meters only):								
Santa Barbara shelf	1977	6	0.04	0.04	0.01	0.07	0.02	1
	1985	4	0.019	0.018	0.015	0.022	0.004	2
Port Hueneme to Point Dume	1977	2	0.042		0.026	0.057	0.022	1
	1985	2	0.05		0.018	0.08	0.044	2
Newport to Dana Point	1977	2	0.024		0.012	0.036	0.017	1
	1985	1	0.019		c			2
Outfall Areas:								
Santa Monica Bay	1977[b]	10	0.234	0.173	0.085	0.499	0.138	1
	1985[b]	3	0.044	0.043	0.037	0.052	0.01	3
Palos Verdes shelf	1977[b]	8	38.6	24.4	0.115	175	57.8	1
	1985[b]	10	16.3	6.88	1.3	56.1	20.5	3
Orange County shelf	1977[b]	5	0.035	0.019	0.003	0.10	0.04	1
	1985[b]	9	0.028	0.007	0.004	0.197	0.06	4
Point Loma shelf	1977[b]	2	0.041		0.001	0.08	0.056	1
	1985[b]	8	0.009	0.004	<.001	0.042	0.01	5
Bays and Harbors:								
Marina del Rey[a]	1984	12	0.054	0.049	0.024	0.121	0.026	6
	1985	12	0.047	0.025	0.009	0.152	0.046	7
	1987	13	0.030	0.026	0.001	0.073	0.021	8
Los Angeles-Long Beach harbors [a]	1973	31	0.51	0.34	0.061	1.98	0.48	9
	1978	31	0.101	0.003	0.001	0.589	0.19	10
Bolsa Bay	1979-80	3	4.62	3.49	3.19	7.18	2.22	12
Upper Newport Bay [c]	1971	3	0.05	0.05	0.01	0.05	0.05	13
Upper Newport Bay[a]	1980	8	0.18	0.14	0.09	0.51	0.13	11
Lower Newport Bay [c]	1971	6	0.02	0.01	<0.10	0.05	0.02	13
OVERALL		**179**			**0.001**	**175**		

[a] - all depths; [b] - 60-m only; [c] DDE only

1 Word and Mearns, 1979	6 Soule and Oguri, 1985	10 Soule and Oguri, 1980b
2 Thompson *et al*, 1987	7 Soule and Oguri, 1986	11 MBC and SCCWRP, 1980
3. Hyperion Treatment Plant, original data	8 Soule and Oguri, 1987	12 Feldmeth, 1980
4 CSDOC, original data	9 Chen and Lu, 1974	13 Young *et al.*, 1975
5 City of San Diego, original data,		

There is evidence that shallow onshore embayments may have been contaminated with DDT from inland sources. Anderson *et al.* (1982) cite a mean tDDT concentration of 0.131 ± 0.05 ppm dw in intertidal sediments collected in August 1971 from six river mouths located between Point Piedras Blancas and Los Angeles. This is in the same range as concentrations in Upper Newport Bay in 1980. In contrast, 1971 concentrations averaged 0.0567 ± 0.034 ppm dw in three more remote river sites including one near Carmel in northern California and two in San Diego County (Anderson *et al.*, 1982). Anderson *et al.* (1982) also note that unlike other coastal samples where limited by DDE, these 1971 river-mouth samples were not, but also contained the most toxic metabolite, o,p'DDT and thus resembled relatively fresh technical grade DDT.

In contrast, most of the lowest concentrations of DDT have occurred in sediments from rural coastal shelf sites with 1977 and 1985 mean concentrations ranging from 0.02 to 0.05 ppm dw. Mean concentrations in sediments of some sites adjacent to urban areas have also been low, for example, off Point Loma (0.009 and 0.041 ppm dw), Orange County (0.028 and 0.035 ppm dw), and in Marina del Rey (0.03 to 0.054 ppm dw; Table 16.1).

Samples taken along the entire coastal shelf at 60 meters in 1977 contained tDDT concentrations ranging from 0.001 ppm dw at a site near La Jolla, to 175 ppm at a site near the JWPCP outfalls off Palos Verdes (Figure 16.2). These data indicated that DDT concentrations were considerably higher northwest of Palos Verdes than at equivalent distances southward and may indicate the northward spread of DDT from the Palos Verdes Whites Point outfall, which was the dominant source in 1977. Concentrations along the Santa Barbara-Ventura coast north and west of Los Angeles were higher (0.05 ppm) than along the comparable transect south to San Diego (0.001 to 0.01 ppm). There were no samples taken at equivalent depths near the offshore islands.

This general pattern of distribution of DDT in nearshore sediments was similar in 1985 (Figure 16.3), with no significant change occurring in mean concentrations at five comparable reference sites between 1977 (0.021 ppm) and 1985 (0.019 ppm). In 1985, concentrations remained highest in Palos Verdes surface sediments (1.4 to 91.6 ppm), but were 3 to 10 times lower than during 1977 (Figure 16.2). A major long-term (15-year) decrease of DDT deposition in surface sediment near the JWPCP outfalls has been independently documented from core profiles (Stull *et al.*, 1986). DDT concentrations before about 1971 were over 400 ppm dw and decreased at the surface (1981) to less than 10 ppm, a trend that closely parallels declining inputs (Stull *et al.*, 1988). Thus, where sediment concentrations were low, they remained relatively unchanged; where they were high, they showed large decreases. The 1984-86 NOAA NS&T Benthic Surveillance and Mussel Watch data agree with the distribution of data from local and regional surveys (Figure 16.4). However, concentrations were even lower than those reported for the SCCWRP 1985 survey.

The overall mean level of tDDT in sediments sampled by NOAA's NS&T Program between 1984 and 1989 was 0.030 ppm dw (median 0.003 ppm dw). This overall average is much lower than levels found in the past at many sites in southern California.

There is considerable disagreement about what concentration of DDT in sediments is toxic to marine life. However, in a survey of sediment toxicity using a 10-day exposure of the amphipod *R. abronius* to Palos Verdes sediments, Swartz *et al.* (1985) reported no toxicity in samples containing 45.0 ppm dw tDDT or less. This is far above current concentrations in most areas, except at several sites along the Palos Verdes coast. However, a more recent study by Anderson *et al.* (1988) suggests a "response concentration" in the range of 0.03 to 0.20 ppm dw. Sediment in this range existed all along the Palos Verdes shelf and in the offshore San Pedro and Santa Monica basins in 1985 (Figure 16.3).

Long and Morgan (1990) estimated effects range concentrations for sediment exposures. The lower 10th percentile of concentrations of tDDT associated with adverse biological effects occurred at 0.003 ppm dw (ER-L). The median concentration associated with effects was 0.35 ppm dw (ER-M). The lower concentration has been detected at most sites in the Southern California Bight. Median levels of DDT only exceeded the ER-M value at Palos Verdes and Bolsa Bay.
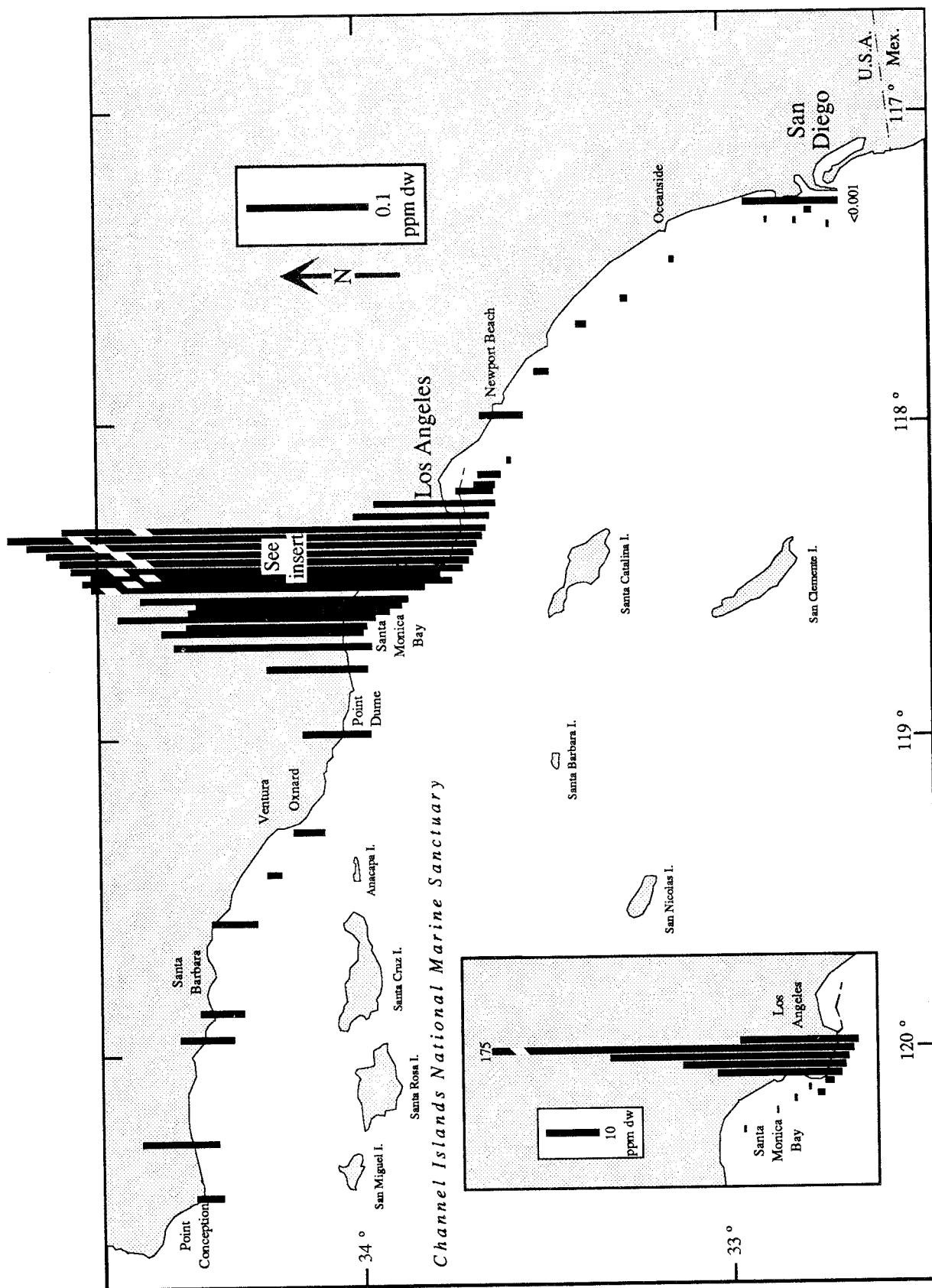
Figure 16.2. tDDT concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line, based on data from the 60-MControl Survey performed from April through August 1977 (Word and Mearns, 1979). Those sites with tDDT concentrations either too low or too high to fit the scale of the columns are indicated by the concentration value in ppm dw (low values) or a broken column with the concentration value (high values).
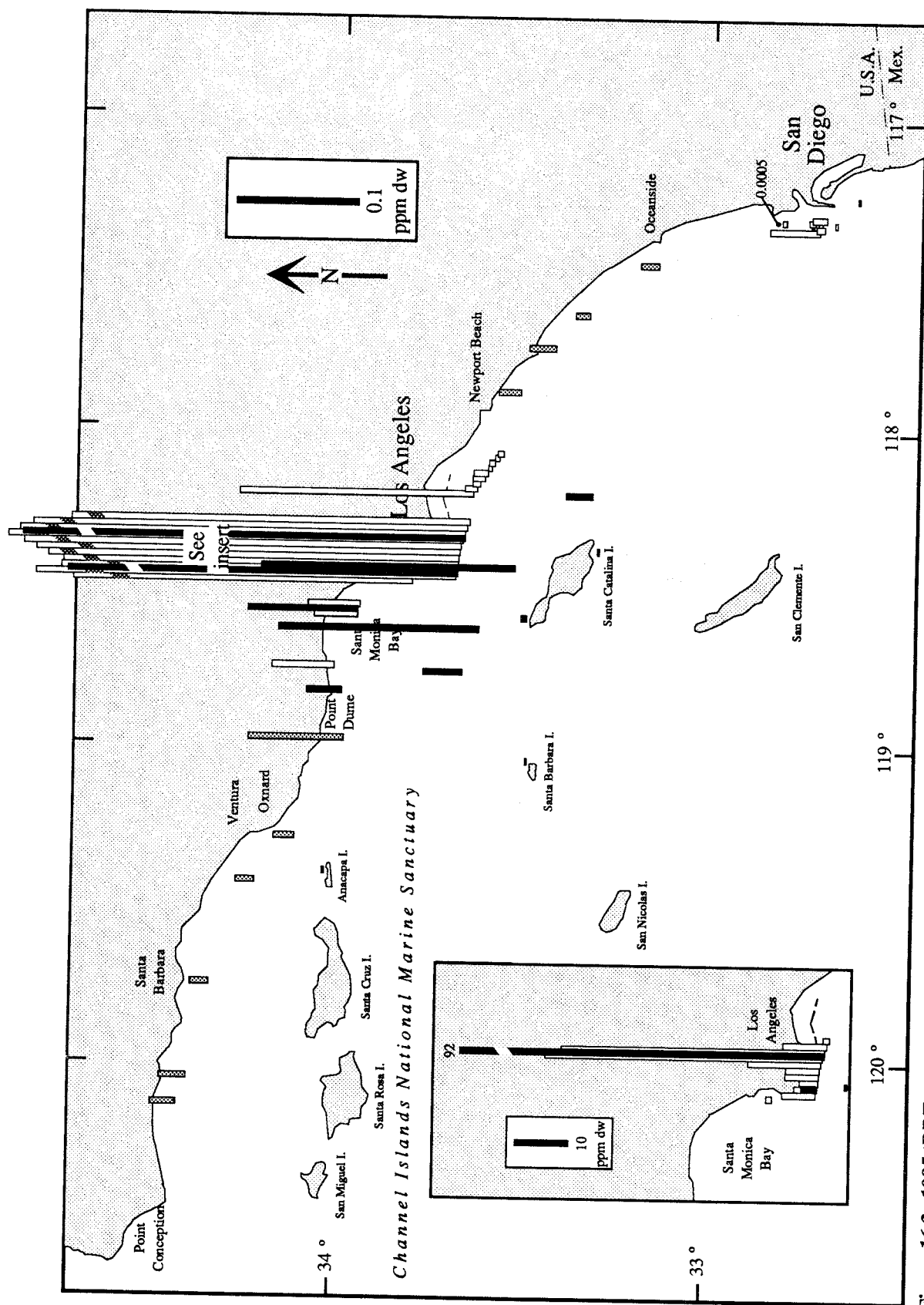
16-5

Figure 16.3. 1985 tDDT concentrations in the surficial sediments of the Southern California Bight along the coastal 60-m contour, in the San Pedro Channel, and off Anacapa, Santa Barbara, and Santa Catalina islands (▮) Thompson, et al., 1987; (▯) various sanitation districts [City of Los Angeles, Los Angeles, Orange, and San Diego counties]). Sites with concentrations greater than 1.0 are indicated by broken bars.
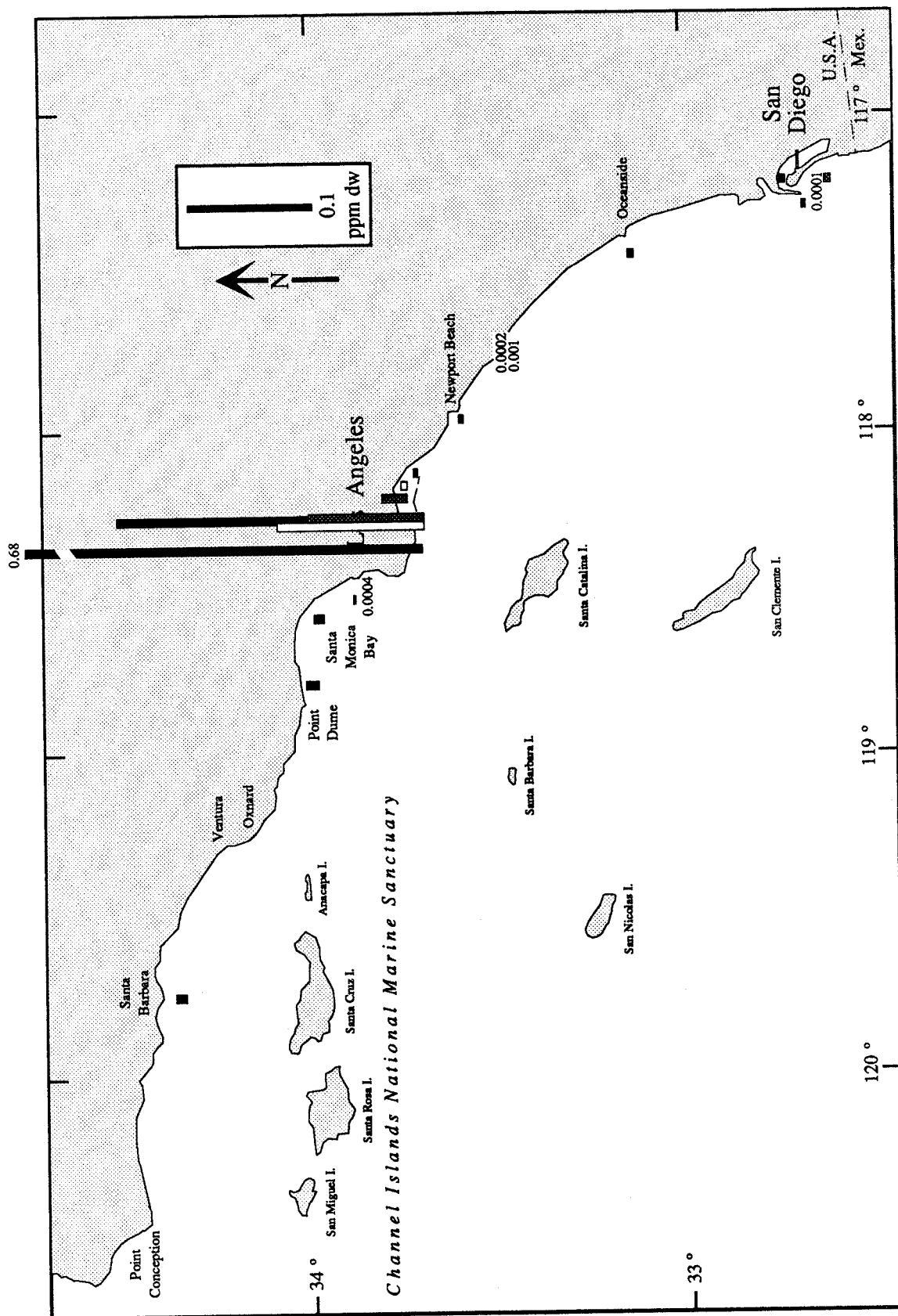
Figure 16.4. tDDT concentrations in the surficial sediments of the Southern California Bight Based on data from NOAA's NS&T Benthic Surveillance Project for 1984 (▯) and 1985 (▨) and Mussel Watch Project for 1986 (▮) (NOAA, 1988 and NOAA, unpublished data).

Concentrations in sediment cores show increases in the Santa Barbara Basin from 1945 to 1967 (Hom *et al.*, 1974) and declines in levels of DDT between 1971 and 1981 at Palos Verdes (Stull *et al.*, 1986).

DDT IN MUSSELS

DDT in mussel tissue has been monitored for many years in the Southern California Bight by a variety of agencies and researchers. Many of these studies overlap in temporal or spatial coverage; unfortunately however, direct comparisons are generally precluded by differences in methods, tissue matrices, and reporting wet weight versus dry weight format. Therefore, while inter-study comparisons are possible for elucidating broad trends, interpretations of absolute concentrations are limited to studies with comparable measurement and analytical parameters. Nevertheless, a 20-year record of monitoring effort (1967 to 1986) exists for the Bight.

Geographic Patterns

In the first synoptic mussel watch survey conducted in 1971 by SCCWRP, concentrations of DDT were highest around the Palos Verdes Peninsula west of Los Angeles-Long Beach harbors. Concentrations appeared to decrease away from this source area. Figure 16.5 shows the distribution of DDT measured in *M. californianus* at 18 sites. Concentrations ranged over 2 orders of magnitude, from 0.04 ppm ww at Santa Barbara and San Clemente Island, to 4.2 ppm at Palos Verdes.

In 1974, SCCWRP repeated its sampling at coastal sites in the Southern California Bight (Figure 16.6), although not all 1971 locations were revisited and some new sites were included. As in 1971, Point Vicente and Royal Palms yielded much higher concentrations of tDDT in *M. californianus* than did any other sites sampled.

Comparable distributions for a major constituent and breakdown product of tDDT, p,p'-DDE, in *M. californianus* and *M. edulis* were obtained by the U.S. EPA in 1976 and 1977 in its Mussel Watch Program (Farrington *et al.*, 1982; Goldberg *et al.*, 1978). Though only seven sites in southern California were sampled, the Los Angeles/Palos Verdes Peninsula region yielded concentrations of p,p'-DDE well above any of those measured at any other location (Figure 16.7). In 1976, *M. californianus* at the Palos Verdes site contained 2.5 ppm ww; the next highest value was measured at Rincon Point, at 0.18 ppm. In *M. edulis*, the difference was even greater: 4.04 ppm in San Pedro Harbor and 0.06 ppm in San Diego Harbor. In 1977, the two highest measured p,p'-DDE concentrations in *M. californianus* were 1.4 ppm at Point Fermin and 0.09 at Oceanside jetty. In *M. edulis*, the two highest values were 0.34 in San Pedro Harbor and 0.04 in San Diego Harbor. Collections made for the LARWQCB in 1982 (Risebrough *et al.*, 1987) can be combined with surveys of mussels from the Baja California coast to provide a broad perspective of DDT contamination in mussels. Figure 16.8 shows that although mussels from the Palos Verdes peninsula contained higher levels of DDT than those from other sites, mussels from the Tijuana area also contained elevated levels of DDT in 1982.

The NS&T Program Mussel Watch Project showed a somewhat different pattern of DDT contamination in the two mussel species in 1986 (Figure 16.9). As was observed in previous studies, elevated tissue concentrations were found in the Los Angeles-Long Beach region (1.06 ppm dw in *M. californianus* at Royal Palms, 1.08 ppm in *M. edulis* at the San Pedro Harbor breakwater), and moderately high levels extended northward into Santa Monica Bay and to Point Dume. *M. californianus* at Point Loma, and especially at Imperial Beach, also exhibited relatively high tissue concentrations of DDT (0.14 ppm and 0.27 ppm, respectively). Sources for these elevated levels are unclear; potential inputs include aerial deposition, or possibly, Mexican sources like the Tijuana River.
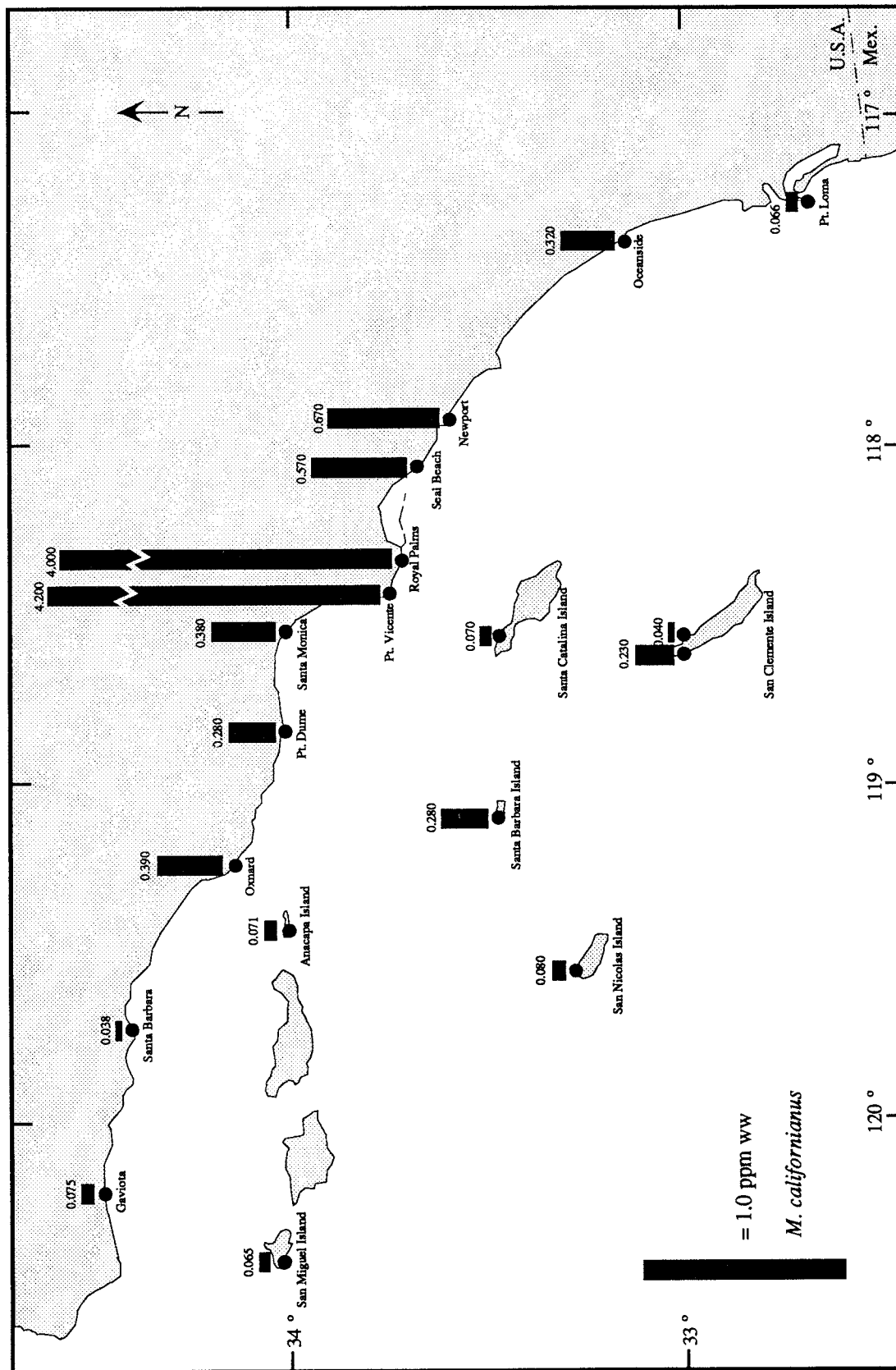
Figure 16.5. tDDT in soft body tissue of mussels, sampled in 1971. Values shown are means of six samples, each sample = one individual. Source: Young, 1974.
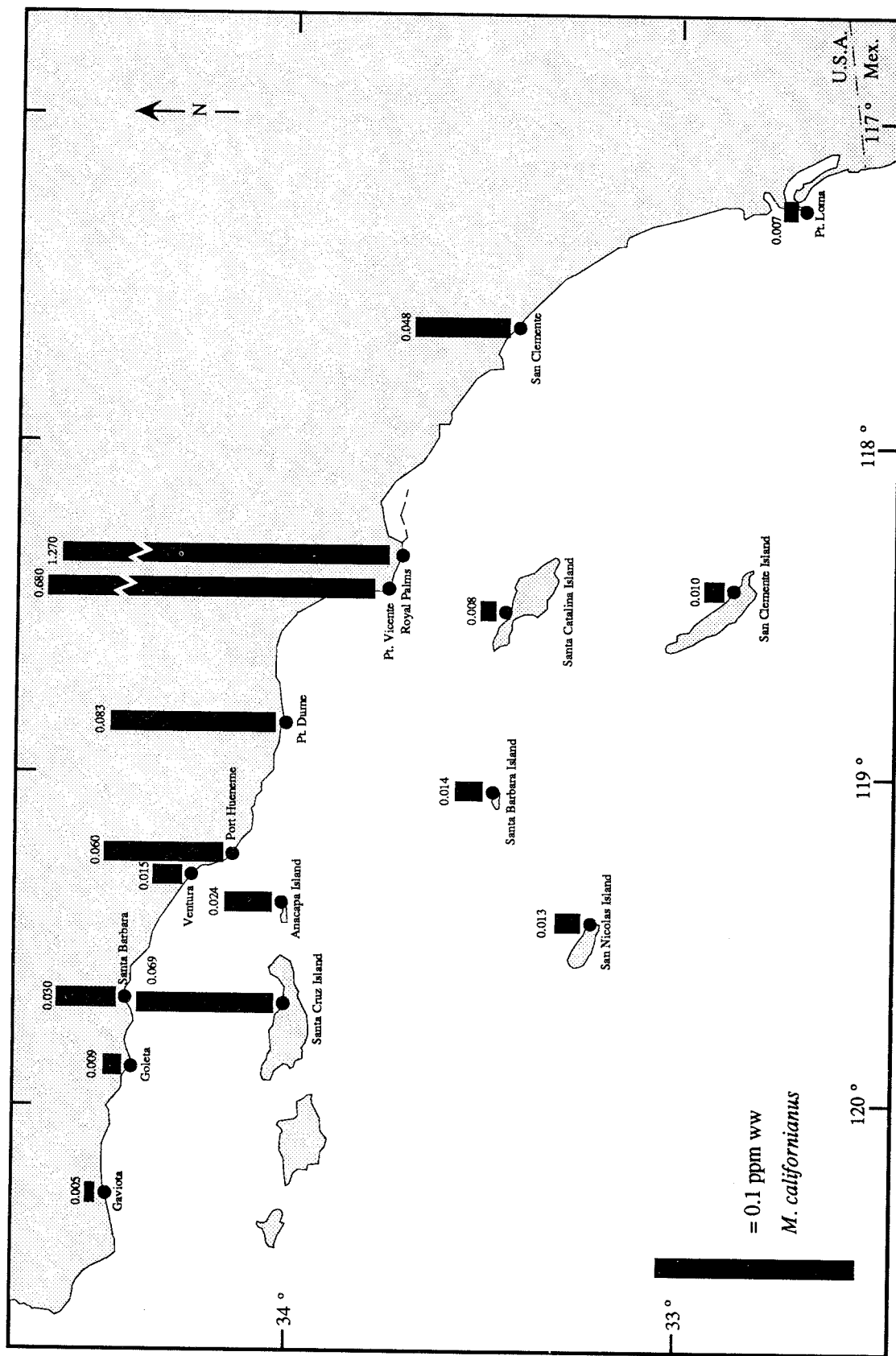
16-9

Figure 16.6. tDDT in soft body tissue of mussels sampled in the Southern California Bight in 1974. Source: Young and Szpila, 1975.
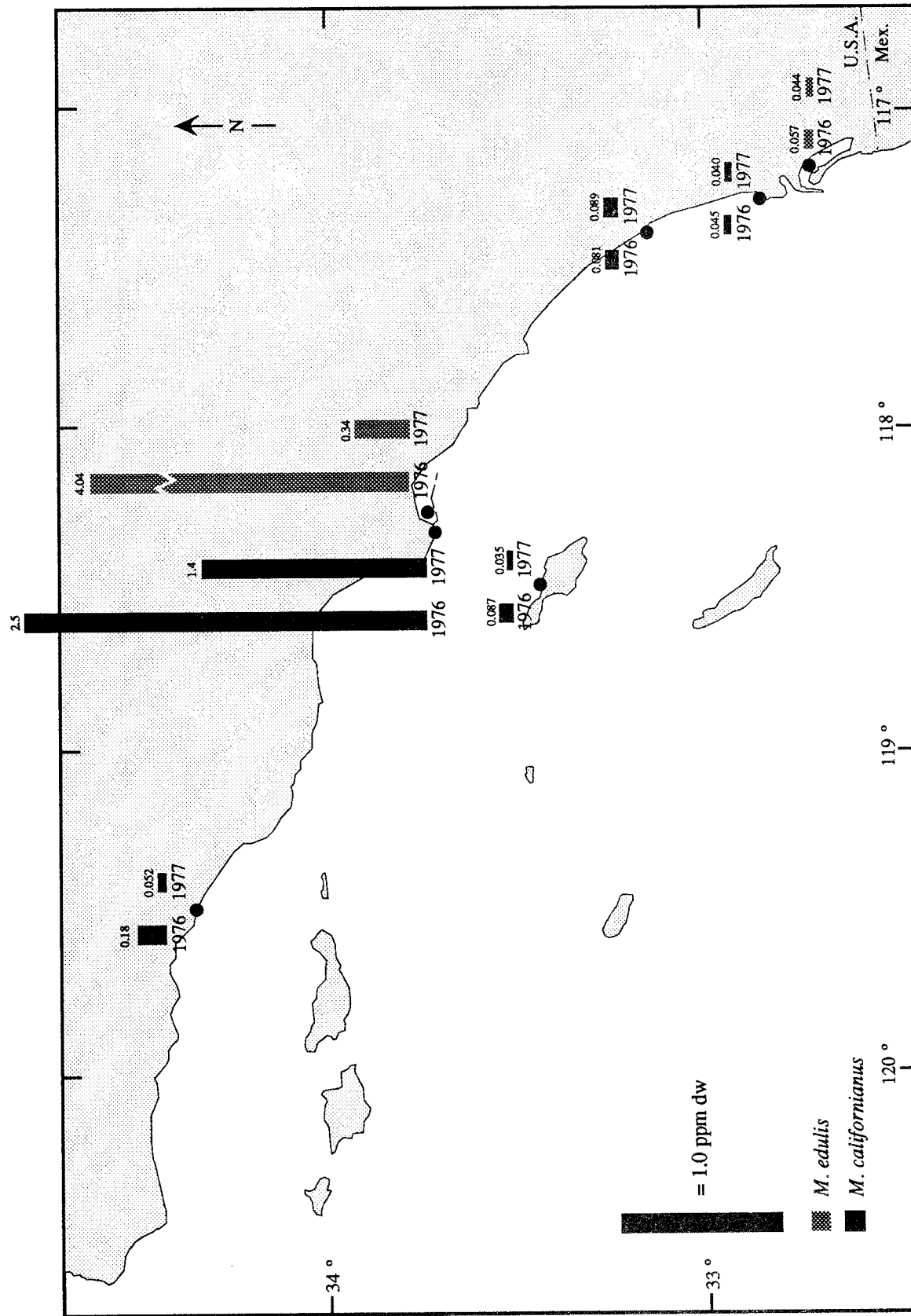
Figure 16.7. p,p'-DDE in whole soft body tissue of mussels, sampled in the Southern California Bight 1976-77. Source: EPA Mussel Watch Program (Farrington et al., 1982).
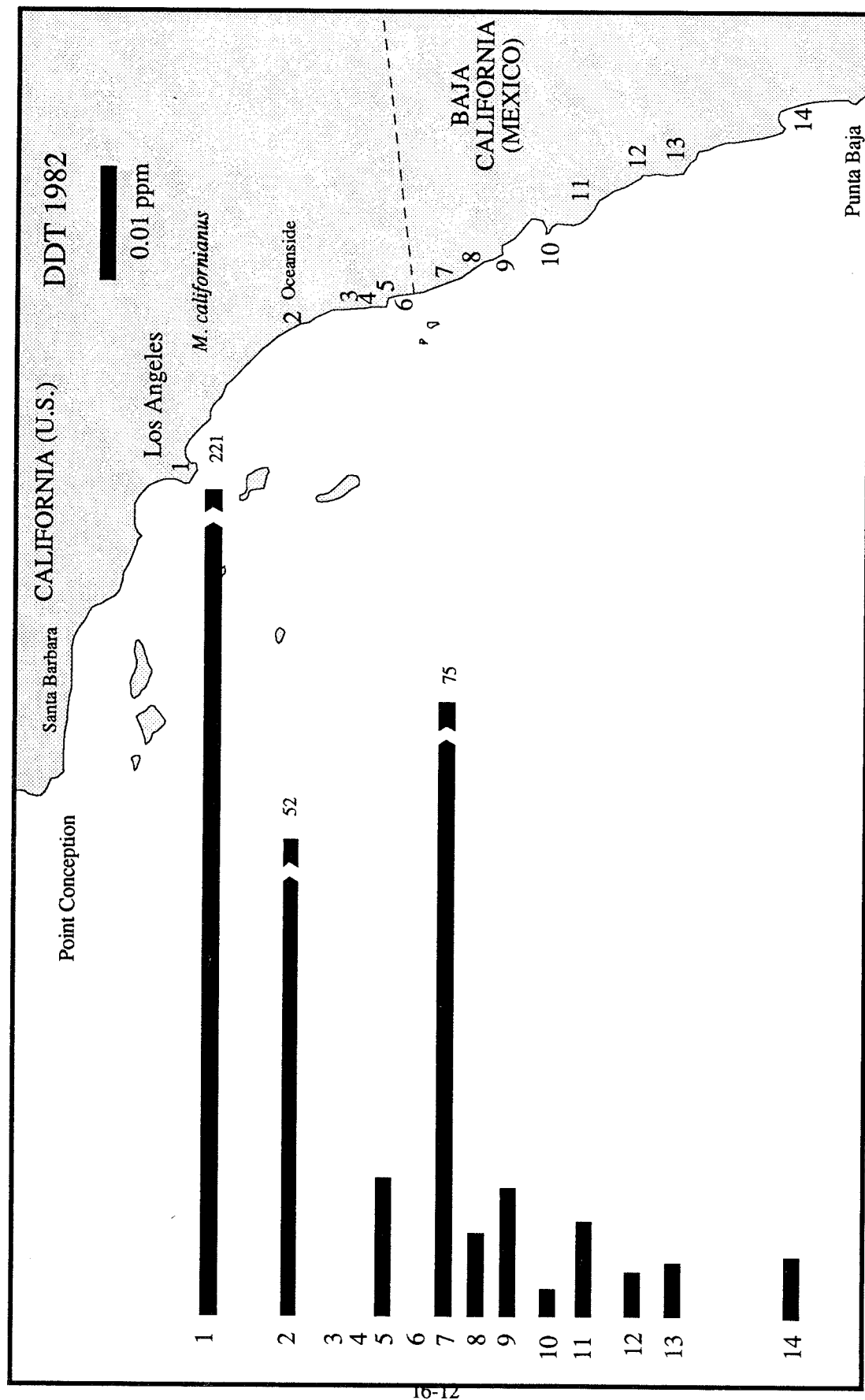
Figure 16.8. Mean DDT concentrations (ppm ww) in mussels from Southern California (Risebrough, 1987) and Baja California (Gutierrez-Galindo et al., 1983a) in 1982.
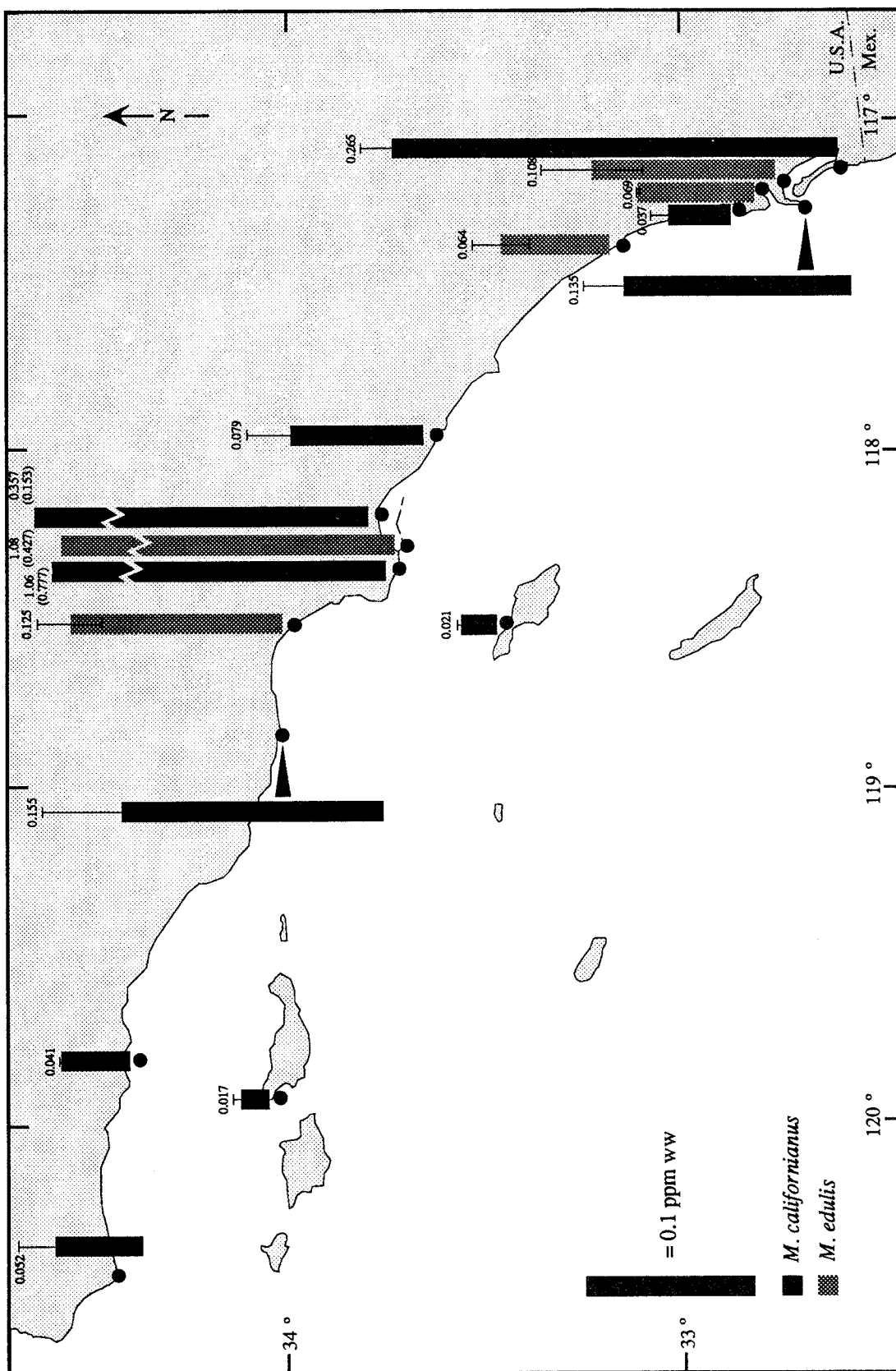
Figure 16.9. tDDT in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

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Distribution of DDT in mussels taken from harbors can be best illustrated using results of a study of harbor pollution in 1974 by SCCWRP (Young and Heesen, 1974). *M. edulis* were analyzed for levels of PCBs (see chapter 15) and DDT (defined as all isomers except o,p'-DDD). Los Angeles-Long Beach harbors demonstrated the greatest range of values and the highest individual measurement for DDT in mussel tissue (1.30 ppm ww). San Diego Harbor, on the other hand, contained extraordinarily low concentrations for an enclosed urban embayment. The range discovered was 0.005 to 0.06 ppm ww, with a median value of 0.03 ppm. This compared with a range of 0.05 to 0.11 ppm and a median of 0.06 ppm measured in *M. edulis* collected outside San Diego. In Newport Bay, an intermediate range of 0.20 to 0.64 ppm ww was measured, but the median value was the highest of the harbors. Young and Heesen (1974) observed that the Newport Bay samples contained roughly twice the levels of DDT as those from the adjacent coast and surmised that because no known point sources existed, recycling of past accumulations within the harbor was responsible. The CMW has since identified San Diego Creek as the most likely source to Newport Bay (Hayes and Phillips, 1986).

Contamination by DDT has been a continuing source of concern in and around San Pedro Bay and in the Los Angeles-Long Beach harbors area. As discussed previously, the ultimate source of nearly all of this DDT contamination was the chemical manufacturing facility located in Torrance. The offshore area near Los Angeles was contaminated by inputs discharged from the JWPCP outfall, while the Los Angeles-Long Beach harbors region apparently also received inputs from storm run-off. Young and Heesen (1974) estimated that run-off into the Los Angeles River was a dominant source of DDT compounds to San Pedro Bay, but that these inputs were relatively small in comparison to those from the submarine outfalls offshore from the Palos Verdes Peninsula. For the Southern California Bight, Young and Heesen (1975) estimated that municipal wastewater input of DDT (primarily from the JWPCP outfall) exceeded that from surface run-off by a factor of 5.

Sampling of resident *M. edulis* mussels by SCCWRP in 1974 supported the observations of Young and Heesen (1975). Mussels collected directly inshore from the JWPCP outfall contained much higher levels of tDDT (1.50 ppm ww) than did those sampled in Los Angeles Harbor in the major stormwater channels of Dominguez Channel (0.26 ppm) and the Los Angeles River (0.12 ppm; Figure 16.10). Mussels from the middle harbor areas (Figure 16.10) also contained elevated levels of DDT.

Los Angeles-Long Beach harbors results from the CMW Program have been used by the SWRCB and the U.S. EPA to require remedial action by the chemical manufacturer responsible for the DDT contamination. CMW sampled 10 sites in the San Pedro Bay region between 1979 and 1985. Several of the inner harbor sites were notable for the elevated concentrations of tDDT found in *M. edulis* collected there, which led to regulatory actions by the LARWQCB and the U.S. EPA.

In the NS&T Mussel Watch Project, sites located in San Pedro Bay yielded two of the three highest concentrations for tDDT in tissues of *M. californianus* and *M. edulis* sampled in the Southern California Bight. The mean value in *M. californianus* at the San Pedro Harbor fishing pier measured 1.08 ppm dw, and in *M. edulis* at Anaheim Bay, 0.36 ppm. Barring new inputs into these areas, or re-suspension of previously contaminated sediments, it would be expected that mussel body burdens of tDDT will continue to decline in subsequent sampling cycles for the NS&T project as they have in other monitoring programs.

Interpretations of results from the CMW Program and the NS&T Mussel Watch Project are made more difficult by the fact that in each survey, only two sites were sampled, with different species collected at those sites. In the CMW Program, *M. californianus* were sampled at Palos Verdes in 1980 and *M. edulis* were sampled at Marina del Rey in 1982. The concentration of 1.6 ppm dw measured near Marina del Rey (*M. edulis*) ranked among the ten highest values encountered for that species in CMW sampling. This result conforms to aerial fallout patterns reported by Young, McDermott, and Heesen (1976a), and may reflect this input mechanism.
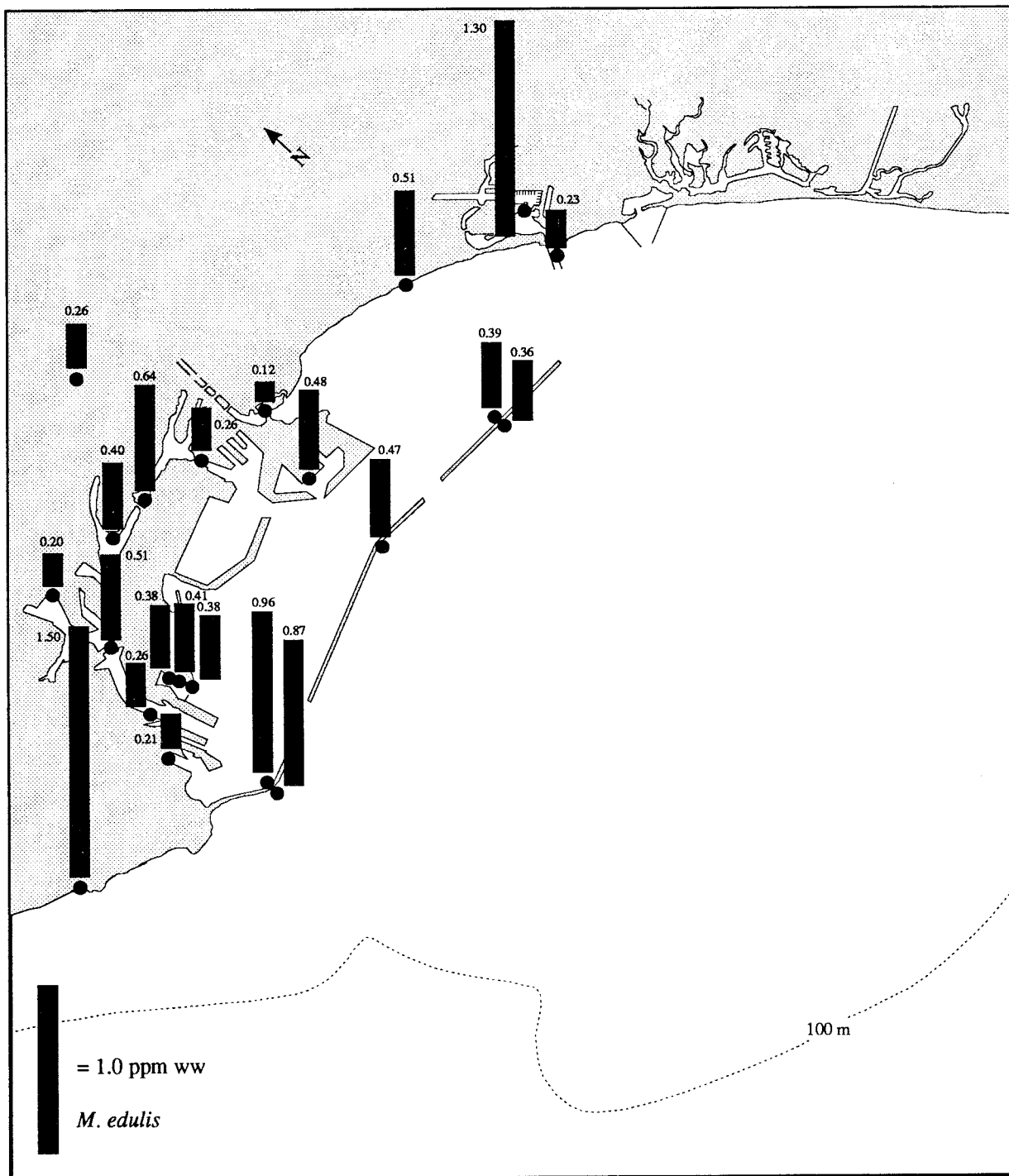
Figure 16.10. Total DDT in mussels sampled in San Pedro Bay in 1974. Source: Young and Heesen, 1974.

Unlike other contaminants analyzed in mussels, tDDT in San Diego Harbor mussels has been relatively low compared to other embayments and coastal regions in the Southern California Bight (Figure 16.11). The 1974 SCCWRP harbors study sampled and analyzed *M. edulis* from San Pedro Bay and San Diego Harbor. Mean tissue concentrations of tDDT in San Pedro Bay exceeded those in San Diego Harbor by an order of magnitude (0.49 ppm ww and 0.04 ppm, respectively). CMW Program results also show a lesser degree of contamination in San Diego Harbor (Shelter Island site) *M. edulis* tissue relative to both Santa Monica Bay and San Pedro Bay. The two Shelter Island concentrations were lower than any of those reported for either Santa Monica Bay or San Pedro Bay.
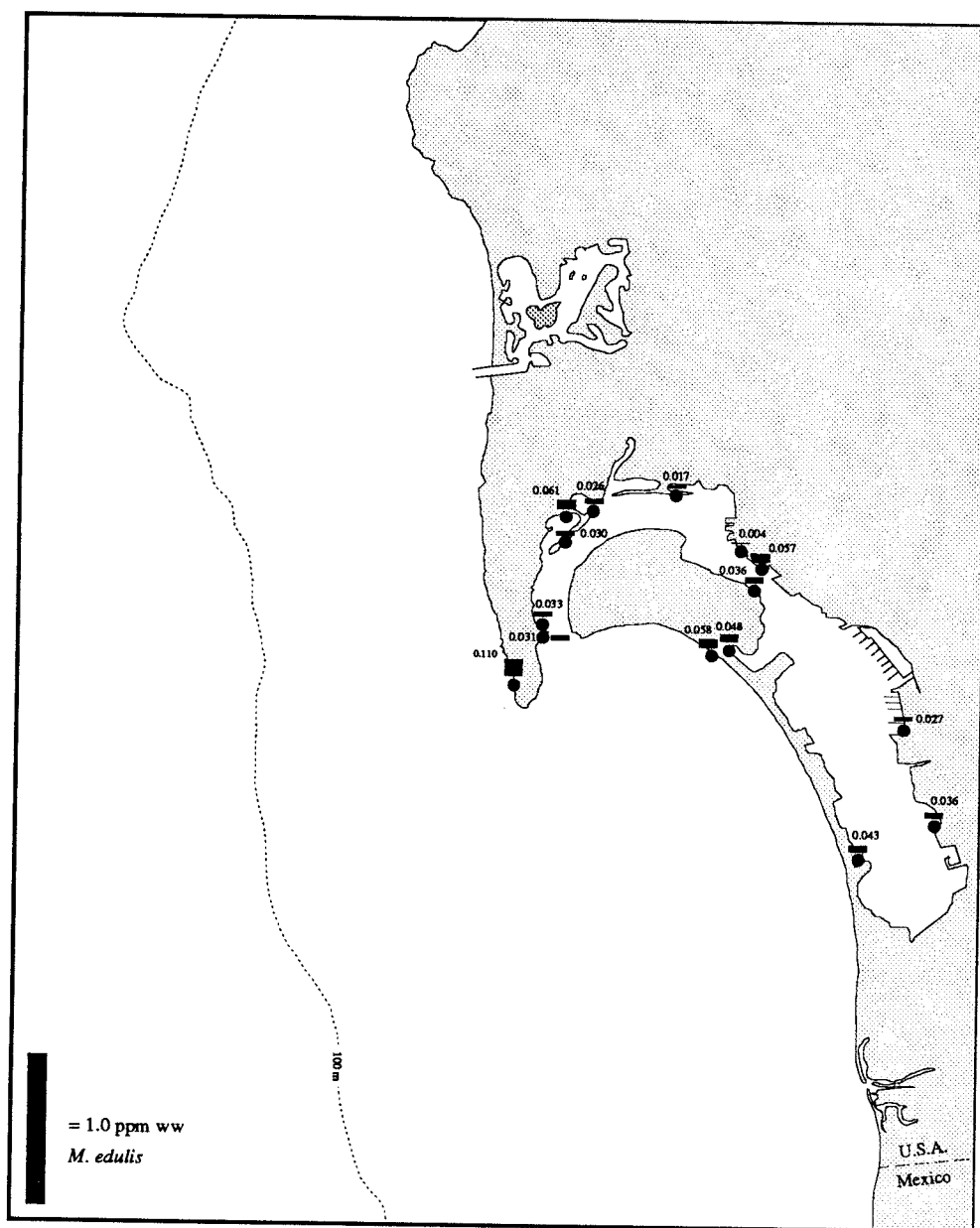
Figure 16.11.   Total DDT in mussels sampled in San Diego Bay in 1974.   Source: Young and Heesen, 1974

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Similar results were obtained in the NS&T Mussel Watch sampling in 1986. Tissue concentrations of tDDT in *M. edulis* sampled at the San Diego Harbor Island site (0.108 ppm dw) ranked lowest among sites in the three major embayments examined in the Southern California Bight. Higher concentrations were measured in *M. californianus* from sites outside San Diego Harbor, Point Loma (0.135 ppm dw) and Imperial Beach (0.265 ppm dw; Figure 16.9). Sources of DDT to these areas may include the municipal outfall offshore from Point Loma, or possibly agricultural application of DDT in Mexico.

Overall mean levels of tDDT in mussels sampled nationwide by NOAA's NS&T Program were similar for *M. edulis* and *M. californianus* (0.113 ppm dw and 0.135 ppm dw, respectively). Median values for the two species were lower: 0.052 ppm dw for *M. edulis* and 0.033 ppm dw for *M. californianus*.

Temporal Trends

Although no single investigator has measured DDT in mussels continually since 1971, trends over time can be pieced together from the wealth of mussel samples taken by SCCWRP, CMW, NS&T, and others.

The NPMP monitored DDT concentrations in Mugu Lagoon, Anaheim Bay, and Hedionda Lagoon monthly between 1965 and 1971, and again in 1977. Butler (1973) and Butler *et al.* (1978) report similar temporal trends for all three sites (Figure 16.12). At each site, concentrations were constant or increased until 1970, after which they began a steady decline. In 1977, the final year of the study, DDT levels in mussels were 0.02 ppm ww at Anaheim Bay and Hedionda Lagoon, but about 6 times higher at Point Mugu (0.13 ppm ww).

Assuming that comparable methodologies were employed by SCCWRP for their two regional surveys, concentrations of DDT measured at the same sites in the 2 years can be compared. The impact of municipal discharges containing DDT residues, and the effects of DDT source control efforts in the Los Angeles area, appear to be reflected in mussel body burden results for Santa Monica Bay (Young and Szpila, 1975 and Young, 1974). Measurements of tDDT and DDE in body tissues of *M. californianus* analyzed in 1971 and 1974 by SCCWRP showed order of magnitude differences between concentrations at Point Vicente, near Palos Verdes, and locations in Santa Monica Bay. However, between 1971 and 1974, absolute concentrations in mussels at Point Dume and Point Vicente declined by amounts ranging from 71 to 84 percent. This is consistent with the decrease in concentrations observed after 1969 in the NPMP results. The decrease in mussel tissue concentrations corresponds well with JWPCP DDT annual mass emission decreases between 1971 and 1974, from 21,500 kg to 1440 kg (McDermott, 1974; Mitchell and McDermott, 1975).

Results from the EPA mussel watch surveys in 1976 and 1977 indicated that at every site, with the exception of Oceanside, concentrations were lower in 1977 than in 1976. At Oceanside, the difference between 1976 and 1977 was negligible. Therefore, the general pattern of highest concentrations center on Los Angeles and of steady decreases in concentration with time that were observed in the NPMP and SCCWRP studies, are supported by EPA Mussel Watch results.

Collections and measurements by the LARWQCB (Risebrough, 1987) and from the CMW Program represent a substantial body of data from which temporal trends of DDT concentrations in mussel tissue may be inferred. Risebrough's analyses of p,p'-DDE concentrations in *M. californianus* cover the period between 1971 and 1986, while CMW results for DDT include more frequent samplings between 1977 and 1986. The two sites sampled by Risebrough that give the greatest temporal coverage are Royal Palms and Santa Barbara Island. Concentrations of p,p'-DDE measured in mussels collected at these two sites plotted against time are illustrated in Figure 16.13. Results from both sites appear to show a substantial decline in mussel DDE levels between 1971 and 1974 and no apparent change between 1977 and 1986. Concentrations measured during equivalent time periods differed about an order of magnitude between the two sites.
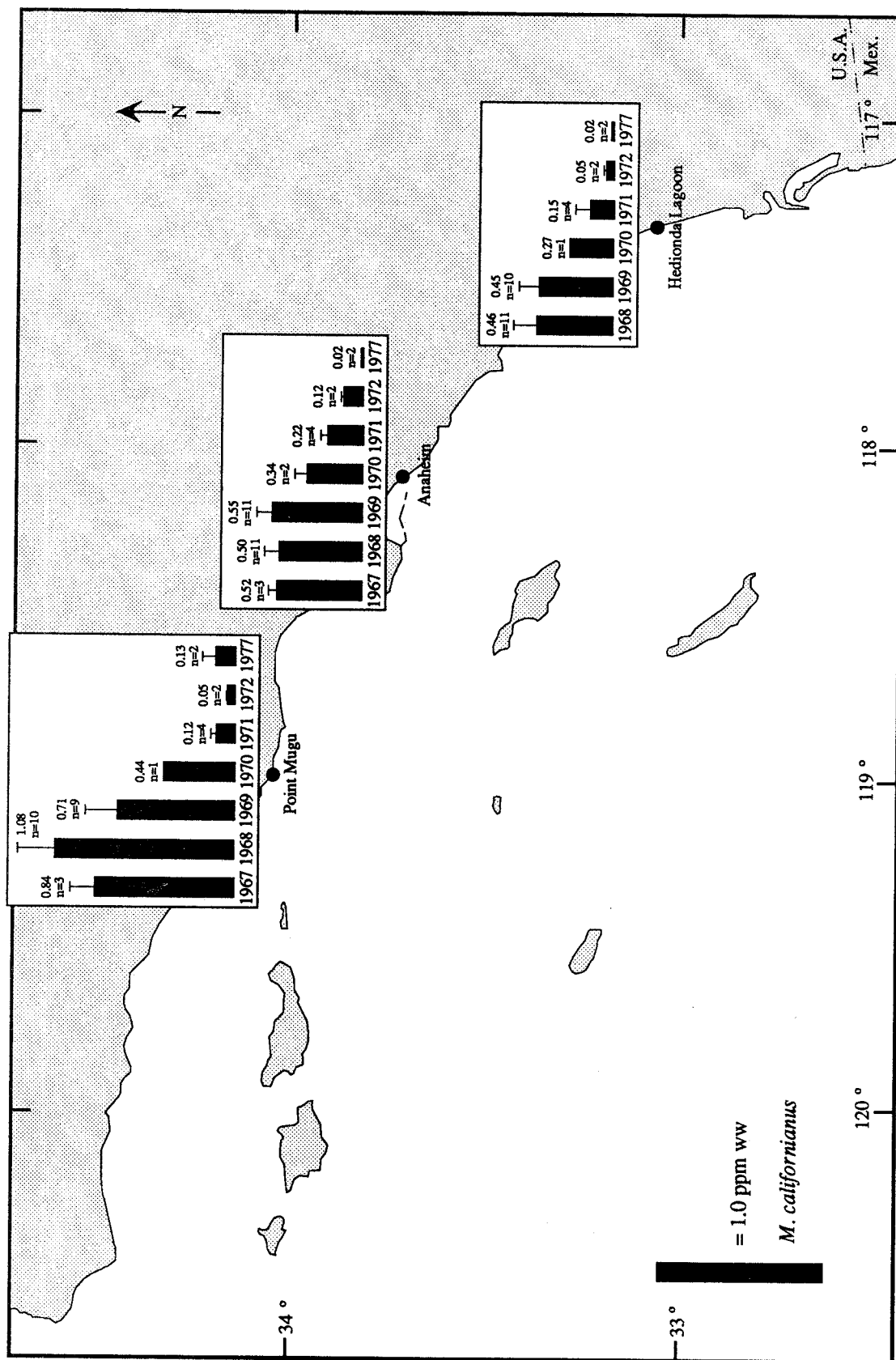
Figure 16.12. Temporal trends of tDDT in soft body tissue of mussels, sampled 1967-1977. Values shown are means of samples collected during each year. Source: Butler, 1973.
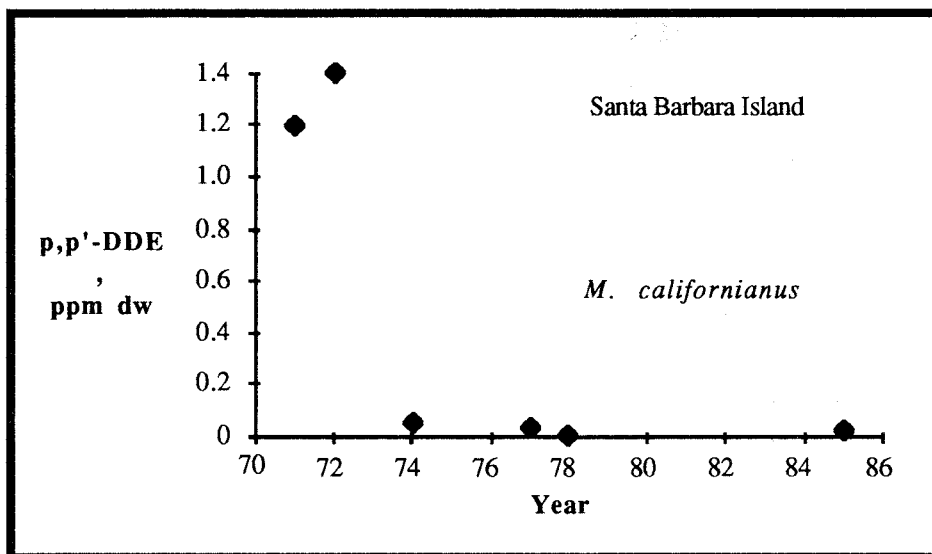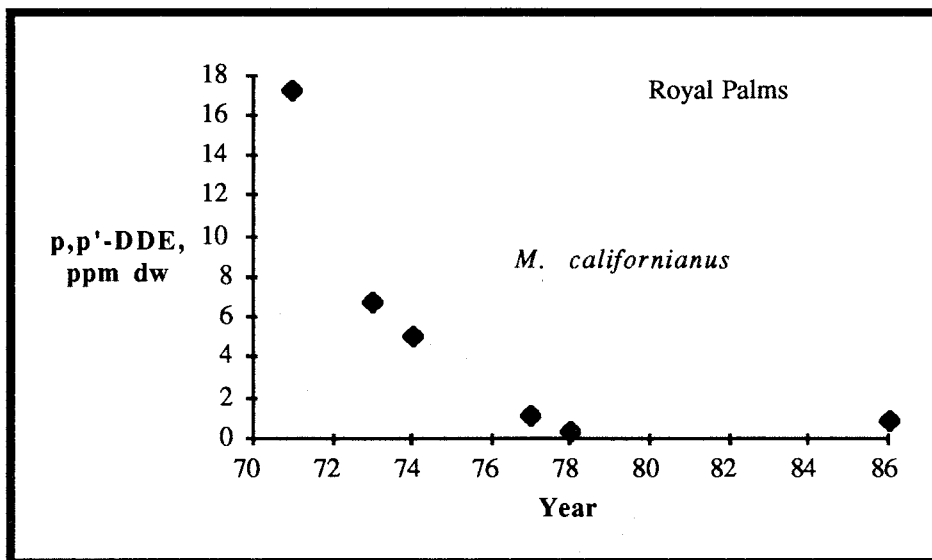
Figure 16.13. Time series of DDE in mussels sampled at Royal Plams and Santa Barbara Island 1971-86. Source: Risebrough, 1987

Conveniently, the period of time for which Risebrough reported the fewest results was a period well covered by CMW. CMW mussel body burden concentrations of DDT and its derivatives are available for the years 1977 through 1985. Figure 16.14 illustrates tDDT results for five sites (note differences in scale and temporal coverage among plots). CMW sites at Royal Palms and Oceanside showed increases in tissue concentrations of tDDT around 1980 and 1981, followed by overall decreases in 1986 (Figure 16.14). At Royal Palms, the measured concentration of tDDT increased from 0.47 ppm dw in November 1978 to 2.26 ppm in October 1979, then declined steadily to 0.51 ppm in December 1985. At Oceanside, levels in resident mussels increased from 0.15 ppm in November 1978 to 0.62 ppm in October 1981, with a December 1985 concentration measured at 0.06 ppm.

Results from the Los Angeles River and Colorado Lagoon (near Long Beach) sites span only the years 1980 to 1985, but appeared to show a downward trend in tissue concentrations of tDDT (Figure 16.14). The Corona del Mar site, in contrast, was sampled between 1977 and 1981 and suggested a general upward trend in concentrations (Figure 16.14). The facts that the Royal Palms site and the Oceanside site reflect the same trend and the concentrations of tDDT showed similar patterns to those for tPCB (see chapter 15) suggest that nonpoint sources may have been responsible for elevations observed in the early 1980s. A possible explanation is that Los Angeles County cleaned its waste system in 1978 that resulted in remobilization of large amounts of contaminants that had accumulated in pipes and catch basins. Also, the period 1978 through 1983 was characterized by unusually heavy rainfall and warm offshore water conditions in southern California, which could have increased run-off and uptake of contaminants. Similarly, Risebrough (1987) noted the temporal results obtained for DDE concentrations and suggested that remobilization of compounds from the contaminated sediments near Los Angeles was the only plausible source of continuing environmental input in those waters.

Based on CMW monitoring efforts using transplanted *M. californianus* (Hayes and Phillips, 1987), as well as the limited time-series data available for resident *M. edulis* summarized below, control and cleanup measures at the manufacturing plant site appear to be having the intended effect of decreasing DDT contamination of mussels within Los Angeles-Long Beach harbors (Hayes and Phillips, 1987). Only one collection and analysis of resident mussels has been made since the Cleanup and Abatement Orders were issued in 1983. The result of this analysis from the Los Angeles River site supports the trend of a decline in tDDT body burdens. However, analyses of resident mussels collected at two sites before the regulatory actions, also suggest decreases with time. Cessation of product manufacturing and the remedial actions at the Torrance plant site have apparently substantially reduced major new inputs into the adjacent marine environments, although continuing, but decreasing contamination by existing reservoirs can be expected for some time.

Between 1986 and 1988 the NS&T program found that tDDT levels did not change significantly at most sites sampled in the Southern California Bight. Concentrations of tDDT in mussels from two sites however (Oceanside and Marina del Rey), appear to have more than doubled between 1986 and 1988 (NOAA, 1989).

Between 1971 and the mid 1980s concentrations of tDDT in mussels appear to have declined dramatically. Concentrations have since leveled off and may be increasing at Oceanside and Marina del Rey.
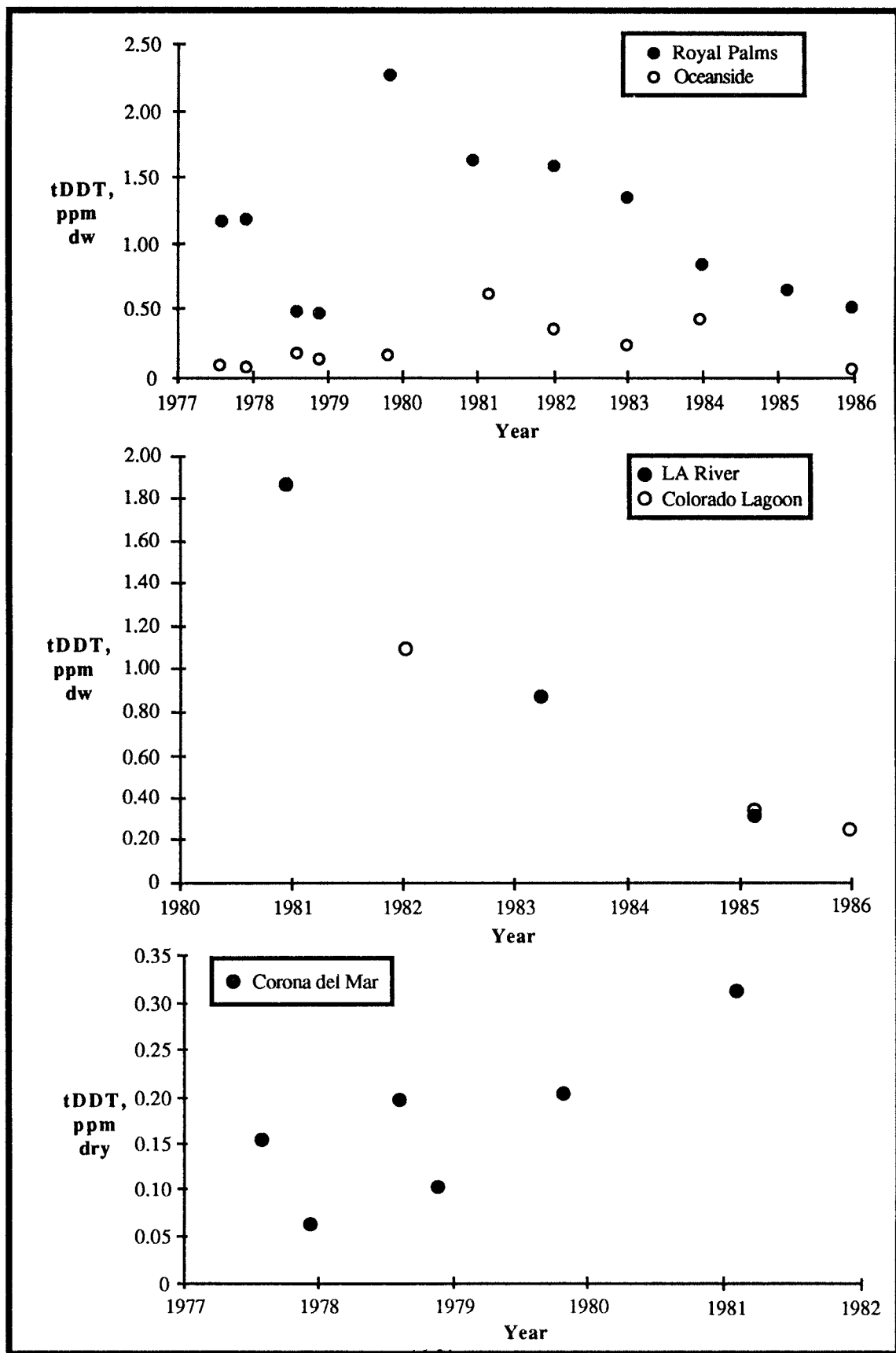
Figure 16.14. Time series of tDDT in southern California mussels sampled in the CMW Program, 1977-85. Note scale differences. Source: Phillips, 1988.

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DDT IN FISH AND OTHER SPECIES

Geographic Patterns

DDT has been measured in thousands of samples of fish, macroinvertebrates, and some seaweeds from the Southern California Bight. To obtain an overview of the geographic range of DDT in a variety of organisms, synoptic survey data for 35 species sampled by one laboratory (SCCWRP) from seven bay, coastal, and island survey areas during the data-rich years 1974 through 1981 were examined. As shown in Table 16.2, mean tDDT concentrations ranged over 4 orders of magnitude in muscle of fish and invertebrates, and in stipe (stalks) of kelp, or whole organisms of other algae, plankton, and mysids. The lowest concentration was less than 0.001 ppm ww in muscle of black abalone from Santa Catalina Island in 1976 and the highest was 176.4 ppm ww in flesh of white croaker collected from the Palos Verdes shelf in 1975. The highest individual measurement was 200 ppm ww in one of the 1980-collected spiny dogfish from Palos Verdes. Other high concentrations occurred in white croaker collected from Palos Verdes during a 1975-77 seafood survey (mean, 39.2 and range 5.23 to 176.4 ppm ww; n = 10); white croaker DDT concentrations were lower in 1980 (mean, 7.63 and range 3.57 to 13.1 ppm ww; Table 16.2). The species least contaminated with DDT was the black abalone, not only for specimens from Santa Catalina Island (less than 0.001 ppm ww), but also for those from the intertidal region of Palos Verdes (mean 0.001, range less than 0.001 to 0.002 ppm ww).

The data reported here are only part of a much larger data base that includes hundreds of additional samples from several discharger monitoring programs and from historical local and federal surveys conducted 1969 through 1976 (Butler and Schutzmann, 1978; Stout and Beezhold, 1981; Munson, 1972; Duke and Wilson, 1971; SCCWRP, 1973). Liver tissue has also been frequently analyzed for DDT content and has usually contained higher levels of DDT than muscle tissue from the same fish. As noted for PCBs (chapter 15), it is likely that some data from these surveys can be used with recent data to reconstruct time series for additional species and locations.

As previously noted, the past heavy contamination by DDT of the area around the Palos Verdes Peninsula has been reflected in sediments and resident bivalves in that region. Similar contamination of fish populations in the area have been documented for a number of years as well. In general, fish from this region were more contaminated (by a factor of 10 to 100 or more) than macroinvertebrates. Mollusks were less contaminated than crustaceans (compare means in Table 16.2).

Geographically, the Palos Verdes area produced the most contaminated mollusks, crustaceans, fish, and sharks. The region with the second highest species mean DDT concentration was Upper Newport Bay where concentrations among six species of fish in 1978 ranged from 0.20 to about 4.25 ppm ww and in 1980, from 0.26 to 2.07 ppm ww (Table 16.3). These fish were slightly more contaminated than a comparable range of species from Los Angeles Harbor collected in 1979 (0.12 to 0.83 ppm ww). Both the Newport Bay and Los Angeles Harbor fish were more contaminated than six species of pelagic fish collected by commercial fishermen from open coastal waters away from Palos Verdes (0.04 to 0.48 ppm ww, mainly in Santa Monica and San Pedro Bays and off Santa Catalina Island; data from Schafer *et al.*, 1982).

Table 16.2. DDT (ppm ww) in marine organisms from the Southern California Bight.

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	SOURCE
Edible Tissues									
Kelp	Los Angeles Harbor	1980	5	0.002	0.001	0.001	0.004	0.001	Mearns and Young, 1980
Alga (Enteromorpha)	Newport Bay	1980	5	0.025	0.025	0.006	0.037	0.013	MBC and SCCWRP,1980
Alga (Ulva)	Newport Bay	1980	5	0.009	0.088	0.054	0.145	0.040	MBC and SCCWRP,1980
Mysids (whole)	Palos Verdes	1980	8	0.302	0.183	0.018	0.575	0.164	Schafer et al.,1982
Zooplankton (whole)	Coastal	1980-81	5	0.008	0.010	0.004	0.010	0.002	Schafer et al.,1982
Black abalone	Palos Verdes	1976	5	0.001	0.001	0.001	0.002	0.000	Young et al., 1978
Black abalone	Santa Catalina Island	1976	3	0.001	~	~	~	~	Young et al., 1978
Gaper clams	Los Angeles Harbor	1979	5	0.036	0.035	0.029	0.043	0.005	Mearns and Young, 1980
Market squid	Coastal	1980-81	3	0.010	0.013	0.006	0.031	0.010	Schafer et al.,1982
Purple hinge scallop	Santa Catalina Island	1973-74	2	0.001	~	~	~	~	Young et al., 1978
Purple hinge scallop	Cortez	1975	8	0.050	0.035	0.001	0.181	0.058	Young et al., 1978
Purple hinge scallop	Palos Verdes	1975/76	9	0.150	0.156	0.096	0.225	0.042	Young et al., 1978
Purple hinge scallop	Dana Point	1976	3	0.004	0.004	0.004	0.005	0.001	Young et al., 1978
Purple hinge scallop	Point Dume	1975-77	3	0.014	0.015	0.011	0.016	0.003	Young et al., 1978
California spiny lobster	Palos Verdes	1976	5	0.563	0.514	0.058	1.490	0.588	Young et al., 1978
California spiny lobster	Santa Catalina Island	1977	3	0.003	0.003	0.001	0.005	0.002	Young et al., 1978
Ridgeback prawn	Santa Catalina Island	1976	3	0.004	0.003	0.003	0.007	0.002	Young et al., 1978
Ridgeback prawn	Palos Verdes	1980	5	0.327	0.283	0.272	0.450	0.077	Schafer et al.,1982
Shore crab	Newport Bay	1980	5	0.050	0.056	0.037	0.061	0.010	MBC and SCCWRP,1980
Shore crab	Newport Bay	1980	3	0.110	0.089	0.071	0.163	0.050	MBC and SCCWRP,1980
Yellow crab	Dana Point	1976	3	0.005	0.005	0.002	0.009	0.004	Young et al., 1978
Spotted sand bass	Newport Bay	1978	3	0.680	0.476	0.199	1.370	0.610	Mearns and Young, 1980
Striped bass	Newport Bay	1978	3	0.690	0.752	0.485	0.823	0.180	MBC and SCCWRP,1980
Barred sand bass	Belmont Pier LA Harbor	1981	3	0.077	0.075	0.057	0.100	0.022	Gossett et al., 1983
Barred sand bass	Orange County	1981	5	0.061	0.052	0.037	0.118	0.032	Gossett et al., 1983
Striped mullet (adult)	Newport Bay	1978	3	4.210	4.390	2.470	5.760	1.650	Mearns and Young, 1980
Striped mullet (juvenile)	Newport Bay	1978	3	1.440	0.998	0.527	2.780	1.190	Mearns and Young, 1980
Striped mullet	Newport Bay	1980	10	2.070	1.555	0.582	4.178	1.315	MBC and SCCWRP,1980
Topsmelt	Newport Bay	1978	3	0.140	0.151	0.125	0.151	0.020	Mearns and Young, 1980
Topsmelt	Newport Bay	1980	10	0.748	0.567	0.099	1.830	0.671	MBC and SCCWRP,1980
White perch	Cabrillo Pier LA Harbor	1981	5	0.196	0.186	0.135	0.283	0.057	Gossett et al., 1983
White perch	Belmont Pier LA Harbor	1981	5	0.176	0.178	0.123	0.219	0.042	Gossett et al., 1983
Black perch	Cabrillo Pier LA Harbor	1981	5	0.160	0.097	0.058	0.311	0.114	Gossett et al., 1983
Black perch	Belmont PierLA Harbor	1981	5	0.263	0.182	0.079	0.713	0.261	Gossett et al., 1983
California corbina	Belmont Pier LA Harbor	1981	4	0.033	0.107	0.020	1.098	0.516	Gossett et al., 1983
White croaker	Palos Verdes	1975	10	39.173	11.160	5.230	176.400	58.520	Young et al., 1978
White croaker	Los Angeles Harbor	1980	5	0.833	0.542	0.336	2.230	0.789	Mearns and Young, 1980
White croaker	Palos Verdes	1980	5	7.629	7.525	3.574	13.083	3.470	Schafer et al.,1982
White croaker	Belmont Pier	1981	5	0.453	0.301	0.209	0.963	0.311	Gossett et al., 1983
White croaker	Cabrillo Pier	1981	4	1.690	1.615	1.102	2.866	0.616	Gossett et al., 1983
White croaker	Dana Point	1981	7	0.185	0.108	0.061	0.465	0.160	Gossett et al., 1983
White croaker	Gerald Desmond Bridge	1981	5	2.810	2.090	0.559	6.588	2.524	Gossett et al., 1983
White croaker	Marina del Rey	1981	5	0.767	0.144	0.116	2.809	1.161	Gossett et al., 1983
White croaker	Navy Mole, LA Harbor	1981	7	1.239	0.282	0.088	6.981	2.542	Gossett et al., 1983
White croaker	Orange County	1981	10	0.125	0.110	0.049	0.273	0.067	Gossett et al., 1983
White croaker	Palos verdes	1981	2	0.000	12.134	3.213	21.054	-	Gossett et al., 1983
White croaker	Queen Mary Long Beach	1981	6	0.228	0.188	0.074	0.539	0.177	Gossett et al., 1983
White croaker	Redondo area piers	1981	5	0.222	0.174	0.095	0.516	0.168	Gossett et al., 1983
White croaker	Santa Monica Bay	1981	5	0.573	0.410	0.167	1.068	0.414	Gossett et al., 1983
White croaker	Santa Monica Pier	1981	5	0.053	0.059	0.033	0.075	0.017	Gossett et al., 1983
White croaker	Santa Monica Bay	1981	5	0.686	0.316	0.126	2.383	0.946	Gossett et al., 1983

Table 16.2. (continued)

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	SOURCE
Mudsucker	Newport Bay	1979/80	3	0.570	0.544	0.189	0.981	0.400	MBC and SCCWRP,1980
Mudsucker	Newport Bay	1979/80	5	0.071	0.059	0.040	0.107	0.030	MBC and SCCWRP,1980
Yellowfin croaker	Newport Bay	1978	3	0.200	0.204	0.174	0.222	0.020	Mearns and Young, 1980
Yellowfin croaker	Newport Bay	1980	10	0.310	0.249	0.148	0.815	0.200	MBC and SCCWRP,1980
Queenfish (whole)	Cabrillo Pier LA Harbor	1981	5	0.238	0.257	0.086	0.328	0.094	Gossett et al., 1983
California halibut	Los Angeles Harbor	1980	4	0.391	0.393	0.336	0.440	0.043	Mearns and Young, 1980
California halibut	Newport Bay	1980	10	0.628	0.649	0.168	1.170	0.277	MBC and SCCWRP,1980
California halibut	Cabrillo Pier LA Harbor	1981	5	0.158	0.137	0.122	0.208	0.037	Gossett et al , 1983
California halibut	Belmont Pier LA Harbor	1981	4	0.131	0.143	0.055	0.184	0.060	Gossett et al , 1983
Flatfish	Belmont Pier LA Harbor	1981	5	0.041	0.039	0.026	0.054	0.012	Gossett et al , 1983
Dover sole	Gaviota	1977	5	0.028	0.025	0.021	0.049	0.011	SCCWRP, unpublished
Dover sole	Rincon	1977	6	0.048	0.042	0.033	0.074	0.016	SCCWRP, unpublished
Dover sole	Malibu Point Dume	1977	6	2.081	1.060	0.204	6.372	2.285	SCCWRP, unpublished
Dover sole	Santa Monica Bay	1977	2	0.313	0.313	0.292	0.333	0.029	SCCWRP, unpublished
Dover sole	Santa Monica Bay	1977	6	1.562	0.660	0.505	5.533	1.974	SCCWRP, unpublished
Dover sole	Santa Monica Bay	1977	5	3.079	0.859	0.829	12.133	5.062	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	39.752	25.652	6.530	123.764	43.699	SCCWRP, unpublished
Dover sole	Huntington Beach	1977	4	0.296	0.255	0.149	0.526	0.179	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	0.126	0.094	0.053	0.222	0.073	SCCWRP, unpublished
Dover sole	Point Loma	1977	6	0.037	0.035	0.020	0.052	0.011	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	19.193	17.889	8.515	30.706	8.725	SCCWRP, unpublished
Dover sole	Palos Verdes	1980	5	7.712	5.990	3.550	12.990	3.580	Schafer et al ,1982
English sole	Rincon	1977	6	0.000	0.061	0.044	0.143	0.041	SCCWRP, unpublished
English sole	Santa Monica Bay	1977	4	1.713	1.428	0.495	3.501	1.283	SCCWRP, unpublished
Sablefish	Santa Monica Bay	1978	5	0.191	0.184	0.160	0.231	0.027	SCCWRP, unpublished
Pacific sanddab	Palos Verdes	1975	19	5.976	5.260	3.040	14.000	2.795	Young et al., 1978
Pacific sanddab	Dana Point	1975	10	0.171	0.157	0.061	0.430	0.105	SCCWRP, unpublished
Pacific sanddab	Palos Verdes	1977	14	23.643	9.216	4.480	75.278	29.520	SCCWRP, unpublished
Pacific sanddab	Palos Verdes	1977	5	13.856	9.429	1.048	61.095	15.710	SCCWRP, unpublished
Pacific sanddab	Santa Monica Bay	1978	6	0.107	0.094	0.044	0.212`	0.059	SCCWRP, unpublished
Pacific sardine	Coastal	1980-81	5	0.484	0.529	0.338	0.591	0.112	Schafer et al.,1982
Rockfish:									
Bocaccio	Santa Monica bay	1981	5	0.058	0.046	0.046	0.072	0.010	Gossett et al., 1983
Bocaccio	Palos Verdes	1980	7	1.057	0.612	0.252	3.940	1.291	SCCWRP, unpublished
Rockfish	Santa Monica Bay	1981	5	0.221	0.184	0.104	0.351	0.114	Gossett et al., 1983
Rockfish	Palos Verdes	1981	5	0.444	0.358	0.234	0.781	0.228	Gossett et al., 1983
Rockfish	Laguna Beach	1981	5	0.036	0.034	0.022	0.048	0.011	Gossett et al., 1983
Lizardfish	Santa Monica bay	1981	5	0.097	0.095	0.051	0.162	0.044	Gossett et al., 1983
Kelp bass	Palos Verdes	1981	5	0.285	0.344	0.055	0.448	0.151	Gossett et al., 1983
California scorpionfish	Santa Catalina Island	1974-75	3	0.097	0.111	0.034	0.146	0.057	Young et al., 1978
California scorpionfish	Palos Verdes	1975	4	3.573	3.515	2.040	5.220	1.409	Young et al., 1978
California scorpionfish	Palos Verdes	1980	4	0.268	0.218	0.028	0.764	0.290	Schafer et al.,1982
California scorpionfish	Santa Monica Bay	1981	5	0.535	0.318	0.045	1.397	0.521	Gossett et al., 1983
California scorpionfish	Palos Verdes	1981	5	0.750	0.758	0.194	1.141	0.577	Gossett et al., 1983
Northern anchovy	Los Angeles Harbor	1980	5	0.121	0.112	0.094	0.175	0.031	Mearns and Young, 1980
Northern anchovy	Coastal	1980-81	5	0.047	0.040	0.021	0.104	0.033	Schafer et al.,1982
Pacific bonito	Coastal	1980/81	5	0.184	0.228	0.068	0.268	0.089	Schafer et al.,1982
Pacific bonito	Whites Point	1981	5	0.116	0.758	0.051	0.183	0.061	Gossett et al., 1983
Pacific bonito	Laguna Beach	1981	5	0.062	0.048	0.029	0.124	0.038	Gossett et al., 1983
Pacific hake	Coastal	1980-81	5	0.036	0.029	0.025	0.055	0.014	Schafer et al.,1982
Pacific mackerel	Santa Monica Bay	1981	5	0.057	0.054	0.024	0.115	0.037	Gossett et al., 1983
Pacific mackerel	Laguna Beach	1981	5	0.129	0.133	0.044	0.263	0.086	Gossett et al., 1983

Table 16.2. (continued)

Common Name	Site	Year	No. of Samples	Mean	Median	Minimum	Maximum	Standard Deviation	SOURCE
Pacific mackerel	Coastal	1980-81	6	0.130	0.051	0.009	0.401	0.145	Schafer et al.,1982
Pacific mackerel	Palos Verdes	1981	1	0.044	-	-	•	-	Gossett et al., 1983
Jack mackeral	Coastal	1980/81	5	0.118	0.072	0.018	0.357	0.140	Schafer et al., 1982
Pacific barracuda	Palos Verdes	1981	5	0.190	0.170	0.056	0.317	0.101	Gossett et al., 1983
Swordfish	Coastal	1980-81	5	0.105	0.056	0.195	0.067	0.009	Schafer et al.,1982
Spiny dogfish	Palos Verdes	1980	5	65.520	44.000	2.700	200.000	79.228	Schafer et al.,1982
Spiny dogfish	Palos Verdes	1981	1	44.020	-	-	•	-	Gossett et al., 1983
Spiny dogfish	Palos Verdes	1981	3	93.660	68.486	14.430	200.056	95.749	Gossett et al., 1983
Thresher shark	Coastal	1980-81	5	0.094	0.090	0.039	0.167	0.048	Schafer et al.,1982
Mako shark	Coastal	1980-81	5	0.143	0.127	0.108	0.198	0.040	Schafer et al.,1982
White shark	Coastal	1980-81	3	0.598	0.585	0.550	0.658	0.055	Schafer et al.,1982
Basking shark	San Pedro	1981	1	<.005	-	-	•	-	Schafer et al.,1982
Blue shark	Coastal	1980/81	1	0.107	0.040	0.008	0.408	0.169	Schafer et al.,1982
LIVER									
Sablefish	Santa Monia Bay	1977	7	11.388	13.174	0.225	20.614	6.239	SCCWRP, unpublished
Dover sole	Gaviota	1977	6	0.878	0.790	0.420	1.419	0.444	SCCWRP, unpublished
Dover sole	Huntington Beach	1977	5	3.096	2.238	1.639	6.786	2.151	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	419.650	182.622	82.628	1588.678	583.628	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	352.074	269.100	80.359	973.784	314.245	SCCWRP, unpublished
Dover sole	Orange County	1977	8	1.170	1.071	0.947	1.478	0.190	SCCWRP, unpublished
Dover sole	Rincon	1977	5	0.633	0.506	0.450	1.064	0.261	SCCWRP, unpublished
Dover sole	Santa Monica Bay	1977	2	7.819	~	4.721	10.916	4.381	SCCWRP, unpublished
Dover sole	Palos Verdes	1977	6	188.106	189.765	140.353	234.201	46.946	SCCWRP, unpublished
Dover sole	Gaviota	1985	2	0.437	0.437	0.399	0.474	0.050	Thompson et al., 1985
Dover sole	Laguna Beach	1985	1	0.460	0.460	-	-	-	Thompson et al., 1985
Dover sole	Tajiguas Point Dume	1985	2	1.513	1.513	0.435	2.591	1.520	Thompson et al., 1985
English sole	Rincon	1977	6	0.901	0.799	0.415	1.769	0.527	SCCWRP, unpublished
English sole	Santa Monica	1977	6	19.754	18.271	16.238	26.235	4.551	SCCWRP, unpublished
Gulf sanddab	Port. Hueneme	1985	1	9.464	9.464	-	-	-	Thompson et al., 1985
Gulf sanddab	Sorrento	1985	1	5.325	5.325	-	-	-	Thompson et al., 1985
Longfin sanddab	Carlsbad	1985	1	6.401	6.401	-	-	-	Thompson et al., 1985
Longfin sanddab	Imperial Beach	1985	1	3.744	3.744	-	-	-	Thompson et al., 1985
Longfin sanddab	La Jolla	1985	1	3.599	3.599	-	-	-	Thompson et al., 1985
Longfin sanddab	Laguna Beach	1985	1	13.190	13.190	-	-	-	Thompson et al., 1985
Longfin sanddab	San Clemente	1985	2	5.372	5.372	2.830	7.914	3.590	Thompson et al., 1985
Longfin sanddab	Sorrento	1985	1	2.419	2.419	-	-	-	Thompson et al., 1985
Pacific sanddab	Santa Monica Bay	1978	6	26.152	27.439	12.796	40.563	9.932	SCCWRP, unpublished
Pacific sanddab	Palos Verdes	1977	6	128.740	140.278	77.902	154.053	28.149	SCCWRP, unpublished
Pacific sanddab	Carlsbad	1985	1	3.275	3.275	-	-	-	Thompson et al., 1985
Pacific sanddab	Imperial Beach	1985	1	3.023	3.023	-	-	-	Thompson et al., 1985
Pacific sanddab	La Jolla	1985	1	6.274	6.274	-	-	-	Thompson et al., 1985
Pacific sanddab	Port Hueneme	1985	1	4.429	4.429	-	-	-	Thompson et al., 1985
Pacific sanddab	San Onofre	1985	2	6.243	6.243	4.230	8.256	2.850	Thompson et al., 1985
Pacific sanddab	Santa Barbara	1985	1	4.701	4.701	-	-	-	Thompson et al., 1985
Pacific sanddab	Trancas Canyon	1985	1	11.494	11.494	-	-	-	Thompson et al., 1985
Pacific sanddab	Ventura	1985	1	4.925	4.925	-	-	-	Thompson et al., 1985

Table 16.3. **Summary of mean tDDT concentrations in muscle of bonyfish from three ecosystem collections sampled between 1974 and 1981. Data from Table 16.2.**

Region	Period	Number of Species	Range in species means minimum	Range in species means maximum
Palos Verdes	1974-80	6[1]	1.06	39.17
Newport Bay	1978	6[2]	0.20	4.25
	1980	6[3]	0.25	2.07
Los Angeles Harbor	1979	3[4]	0.12	0.83
Coastal pelagic	1980-81	5[5]	0.04	0.48

[1] Bocaccio, California scorpionfish, Dover sole, Pacific sanddab, white croaker.
[2] Topsmelt, yellowfin croaker, spotted sand bass, striped bass, striped mullet.
[3] Topsmelt, longjaw goby, striped mullet, yellowfin croaker, striped bass, California halibut.
[4] Northern anchovy, white croaker, California halibut.
[5] Northern anchovy, Pacific sardine, Pacific mackerel, Pacific hake, Pacific bonito, and swordfish.

In an early survey, Valentine (1972) and Valentine and Soule (1973) reported concentrations of DDT in 95 whole barred sand bass collected in five sampling regions in Baja California and southern California between 1969 and 1971. Average concentrations increased with latitude 132-fold from 0.086 ppm ww in 16 fish from southern Baja California to 11.356 ppm ww in 2 fish from the Los Angeles area (site not specified). The large-scale geographic gradient was similar to that reported by Duke and Wilson (1971). However, even though low concentrations were in the same range as those reported by Duke and Wilson (1971) and others cited in Valentine (1972), the authors expressed concern about the absolute concentrations. Re-analysis in 1972 of extracts of six fish from San Clemente by CSDLAC (unpublished data) produced a mean concentration of 0.431 ppm ww, which is lower by a factor of 5.3 than the mean value of 2.298 ppm ww for all 30 fish initially analyzed by Valentine (1972).

DDT concentrations in fish were also of concern in Mexico (Velarde-Rodriguez, 1973). Based on data in Velarde-Rodriguez, and assuming a dry tissue content of 40 percent, it is estimated that livers of spawning adult white seabass (*Atractoscion nobilis*) captured in 1972 around the Coronado Islands contained a median tDDT concentration of about 120 ppm ww (range 20 to 170, n= 7). Gonads contained equally high concentrations (median, 97; range 3.7 to 205 ppm ww; n=10, computed from Velarde-Rodriguez, 1973). These concentrations exceeded the concentration range of 3 to 5 ppm ww in the gonad or liver that have been suggestedto induce sterility and reproductive effects in other croakers (Childress, 1971) and in cutthroat trout (Allison *et al.*, 1964).

Although data for concentrations of DDT in fish tissue are available for a number of species, the species (kelp and barred sand bass) were selected as the basis for discussion here because of a recent extensive survey by the LARWQCB (Risebrough, 1987) and because barred sand bass is included in the NOAA NS&T Program and in other NOAA-sponsored studies. Their relatively large sample size, importance as a fishery (CDHS, 1991), and the availability of results from these species for other contaminants such as PCBs make them a representative and useful target species for analysis.

DDT was measured in muscle of kelp bass from 10 sites in 1985 by LARWQCB and CSDLAC (Figure 16.15). Concentrations decreased sharply with distance from the Palos Verdes Peninsula. Site averages ranged from 0.02 ppm in fish from the east end of Santa Catalina Island, to 1.21 ppm in fish from Whites Point (Figure 16.15). In no case did individual fish exceed the FDA action limit of 5.0 ppm ww in muscle tissue. This may be contrasted with conditions in the early 1970s, when many kelp bass contained muscle DDT concentrations exceeding 5.0 ppm ww (Smokler *et al.*, 1979).
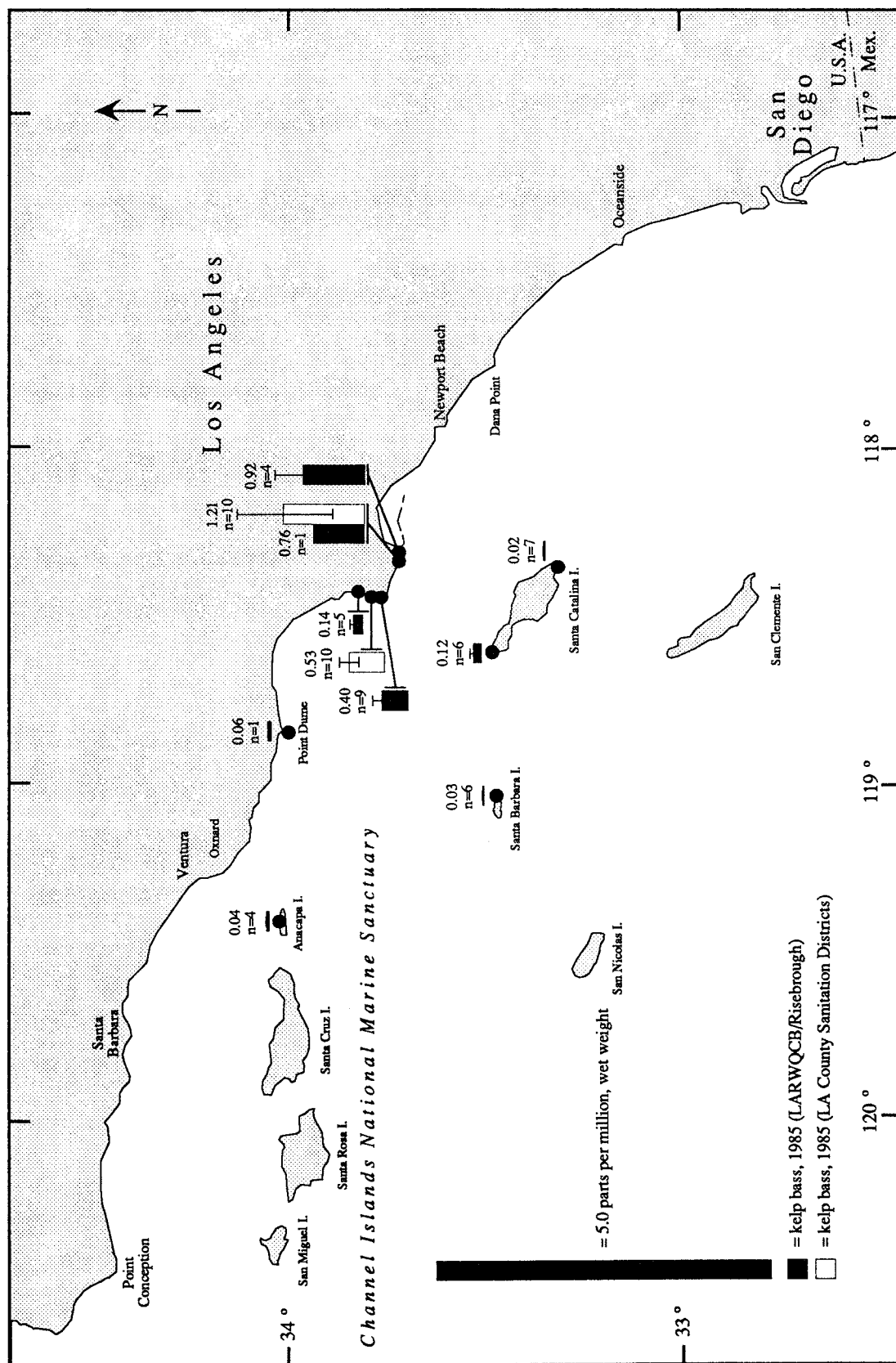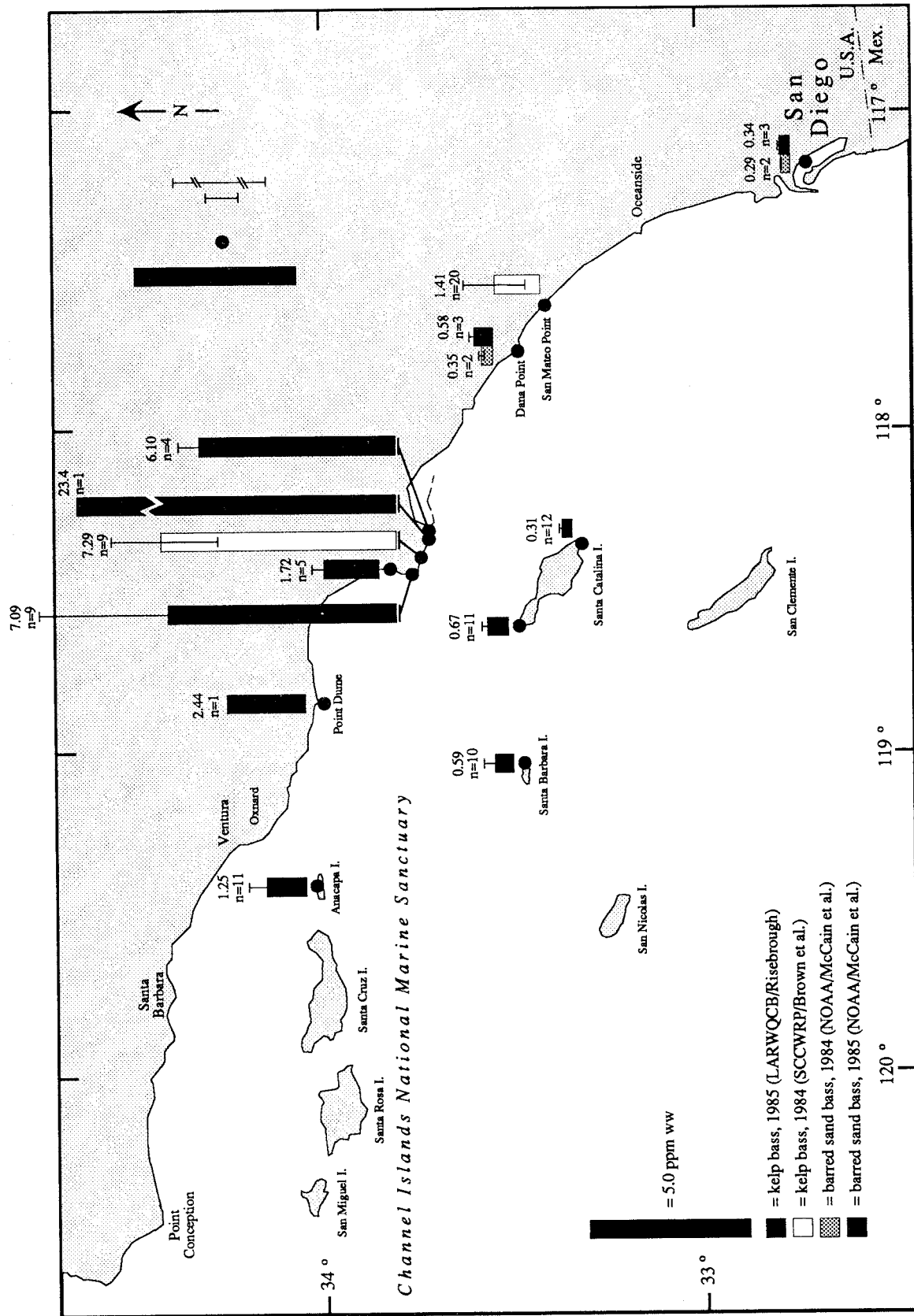
Figure 16.15. Wet weight concentrations of tDDT measured in muscle tissue of kelp bass sampled in the Southern California Bight in 1985. Source: Risebrough (1987); CSDLAC (unpublished).

Although concentrations of DDT in fish muscle may be of concern for human health reasons, concentrations in fish liver have been much higher, possibly high enough to cause adverse health effects for fish. For example, mean concentrations of DDT in livers of rockfish were found to be as high as 349 ppm ww in Santa Monica Bay in 1970 and concentrations around this area exceeded 5.0 ppm ww in various fish as far offshore as Cortez Bank (100 km) and along the coast from northern Baja California to central California (Duke and Wilson, 1971; Figures 16.16 and 16.17). The highest individual concentration in liver of rockfish from southern Santa Monica Bay was 1026 ppm ww. The area of contamination of fish above 5 ppm ww, therefore covered an area of millions of square kilometers. More recent surveys, reviewed below, point to temporal trends of decreasing tissue DDT concentrations in fish, with spatial trends of relatively higher levels of contamination with increasing proximity to Palos Verdes still evident.

DDT was measured in livers of kelp bass and barred sand bass from 13 sites in 1984 and 1985 by LARWQCB, SCCWRP, and the NOAA NS&T Program. Lowest levels were found in fish collected farthest south of the Palos Verdes area, and highest levels were in fish from Palos Verdes (Figure 16.18). Average site concentrations ranged over two orders of magnitude, from a low of 0.29 ppm ww in barred sand bass from San Diego Harbor, to 23.4 ppm in the liver from a single fish from Whites Point. Fish from other areas along the Palos Verdes Peninsula contained average DDT concentrations ranging from 6.10 ppm at Point Fermin, to 7.29 ppm at Bunker Point (Figure 16.18).

Patterns of DDT contamination found by the 1984 NOAA NS&T Benthic Surveillance Project are broadly consistent with the distribution of DDT in bass discussed above. For example, concentrations were highest, on a relative basis (about 6.0 ppm ww), in hornyhead turbot from San Pedro Canyon; moderate (about 2.3 ppm ww) in fish from Santa Monica Bay; and low (about 1.0 ppm ww) in fish from Dana Point and San Diego Harbor (Figure 16.19). White croaker results were consistent with this pattern. Thus, while limited to a few sites, the NS&T data reflected a consistent pattern of the spatial extent of DDT contamination in fish livers.
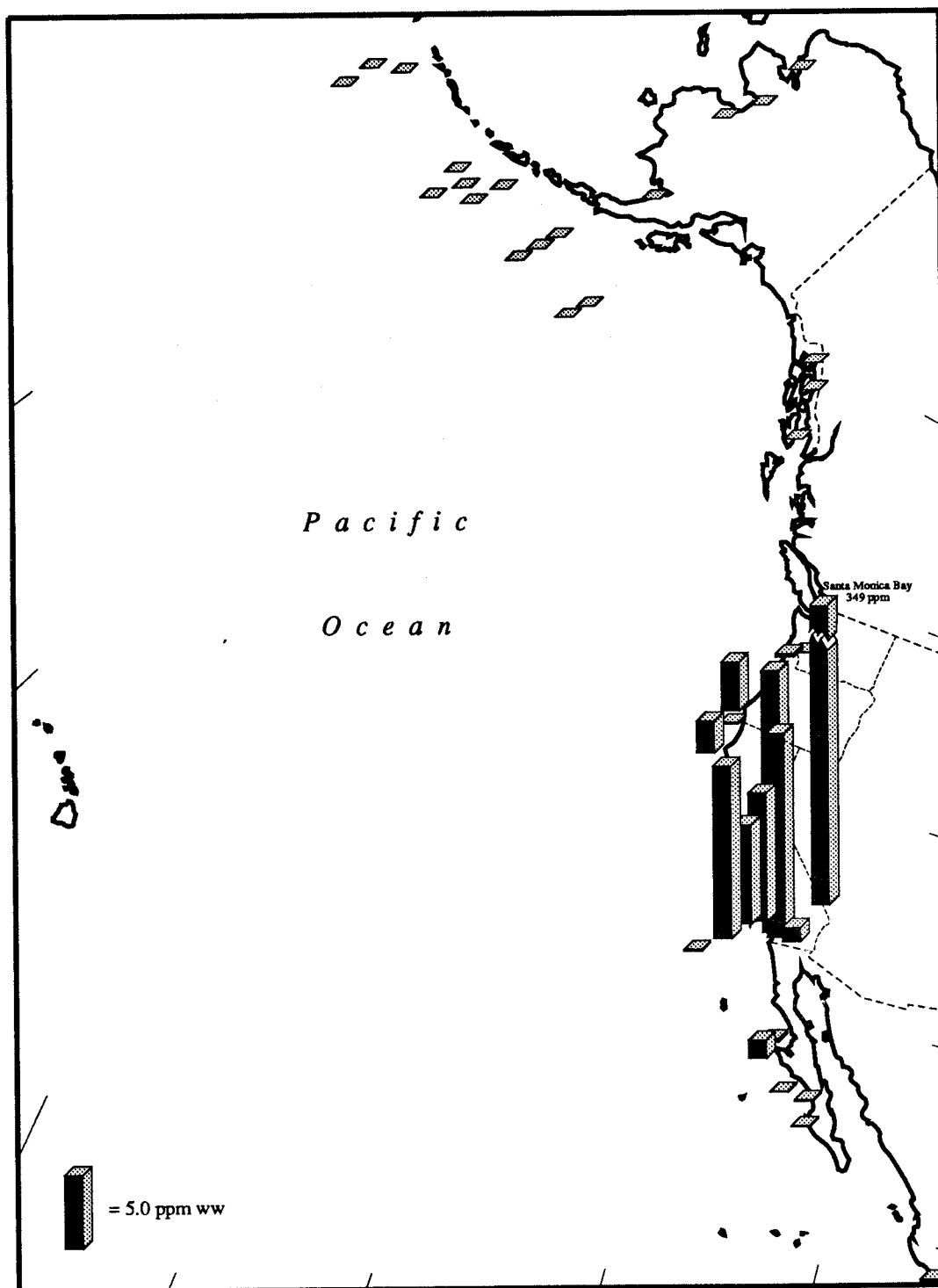
Figure 16.16. Total DDT in livers of fish from various sites in the n ortheast Pacific Ocean during 1970. Bar represents given value and mean. Species vary among sites. Source: Duke and Wilson (1971).
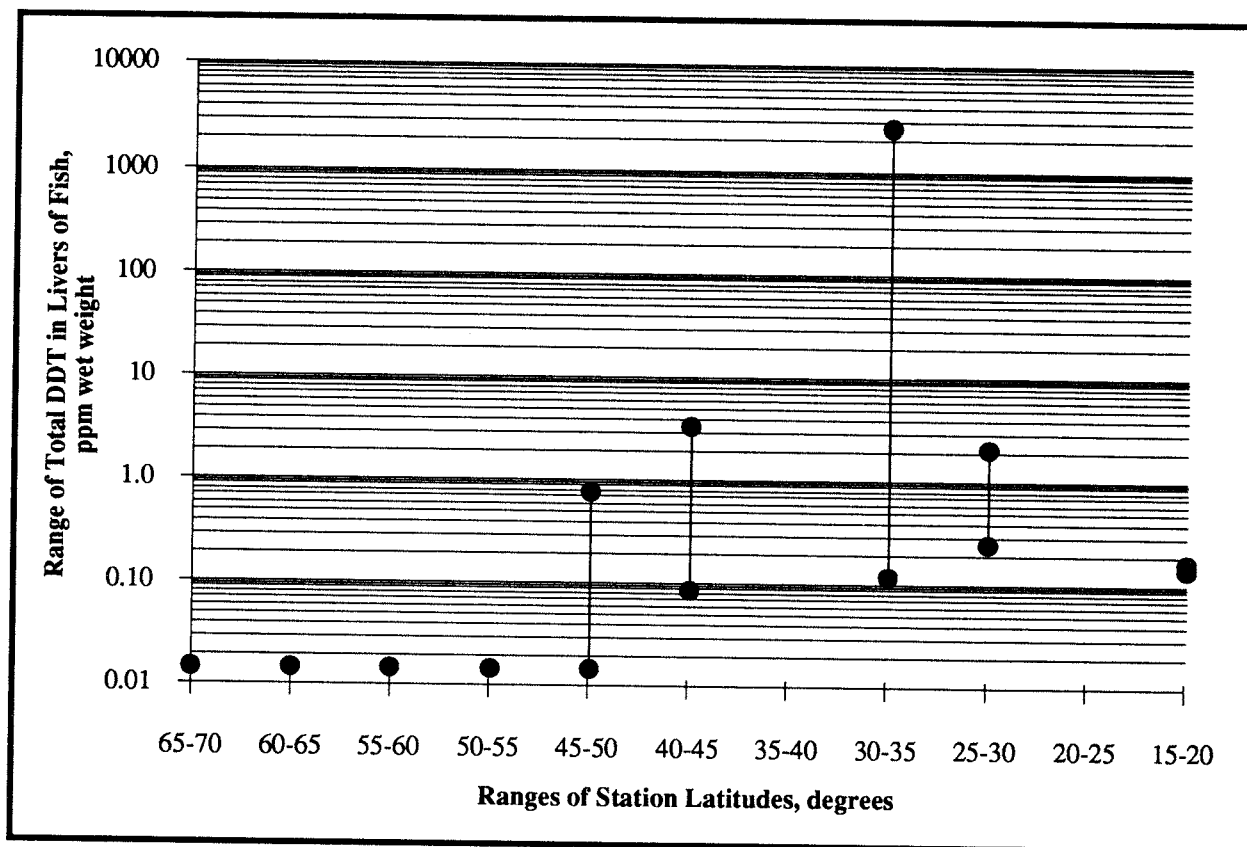
Figure 16.17. Ranges of tDDT concentrations measured in livers of miscellaneous Pacific Coast fish species plotted against ranges of collection latitudes. Source: Duke and Wilson (1971).

Figure 16.18. Wet weight concentrations of tDDT measured in liver tissue of bass species sampled in the Southern California Bight in 1984 and 1985. Sources: Risebrough (1987); Brown et al. (unpublished); McCain et al. (1987); McCain et al. (unpublished).
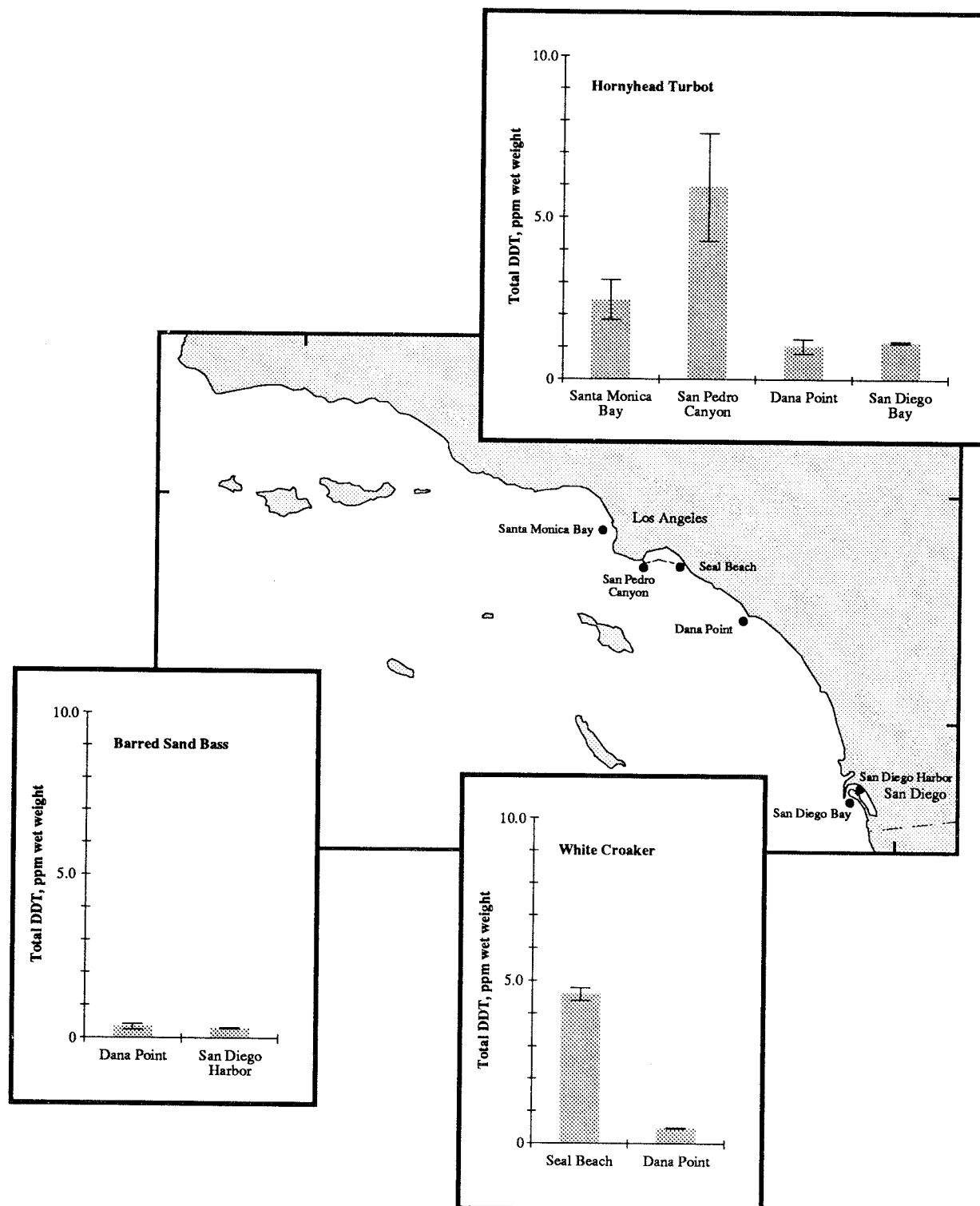
Figure 16.19. Concentrations of tDDT measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi, *et al.*, 1988.

Temporal Trends

There are several data sets that can be used to track the temporal trends of DDT contamination in fish of the Bight. To track the early history of contamination, MacGregor (1974) employed a unique approach to the assessment of temporal trends of DDT in fish off the coast of southern California. Rather than collecting fish on a regular basis and analyzing DDT content in those samples relatively shortly after collection, MacGregor analyzed specimens of the myctophid fish, *S leucopsarus*, from existing preserved collections of the California Cooperative Oceanic Fisheries Investigations (CalCOFI). The preservation of the fish in formalin apparently had no significant effect on the tissue pesticide concentrations (MacGregor, 1974). This enabled the evaluation of DDT body burdens in the fish over a much more extensive period of time--1949 to 1972--than would otherwise be possible. It also afforded the opportunity to assess changes in DDT concentrations over the period of time that the Montrose Chemical plant began DDT manufacturing and waste disposal operations in the Los Angeles area, through its years of peak production, and into the period of imposed restrictions on manufacture, use, and disposal.

Figure 16.20 (from MacGregor, 1974) portrays discrete time periods in the Southern California Bight (1950-52; 1953-56; 1957-60; and 1961-66), and show the progressive increase of the DDT contamination, especially in nearshore fish. Figure 16.21 portrays MacGregor's data for selected stations located around the Palos Verdes Peninsula for which relatively good temporal coverage was available. In all cases, increases in DDT concentrations in the myctophid fish were observed between 1950 and 1962.

More recent analyses of DDT in fish tissue complement the early trends analysis of MacGregor and generally reflect the history of activities at Montrose. Monitoring efforts by CSDLAC offer the longest recent continuous time series (1971-88) of direct measurements for DDT in fish tissue in the southern California region. In 1979, Smokler *et al.* (1979) examined CSDLAC results from the period between 1970 and 1977. They concluded that for three species of fish (kelp bass, Dover sole, and black perch; Figure 16.22) collected near the JWPCP Whites Point outfall zone, median muscle tissue decreases in DDT were either small, or in the case of Dover sole, increased from 1971 to 1975. However, more recent data show that median levels of DDT in Dover sole muscle have declined since 1975 (Figure 16.23).
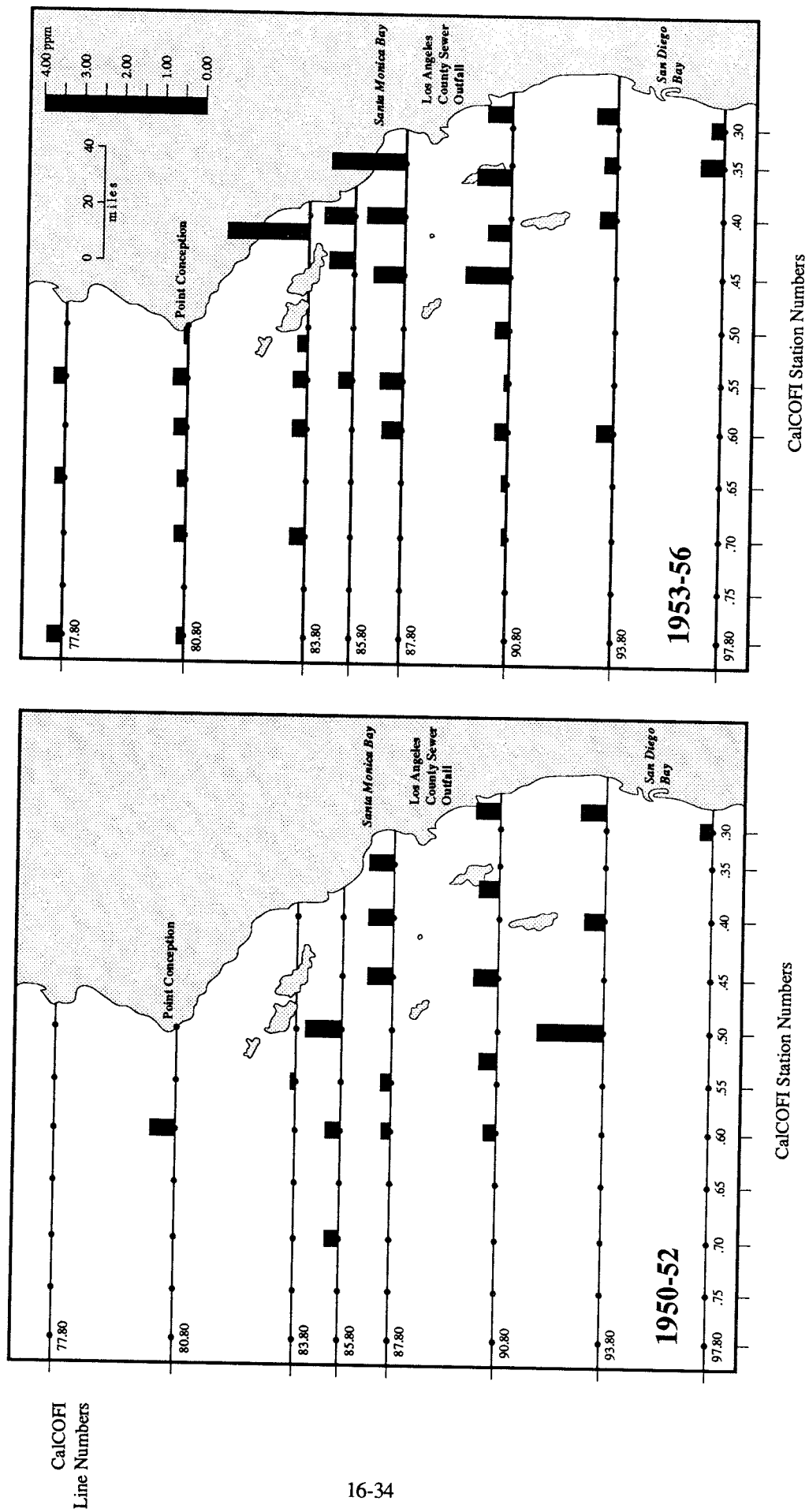
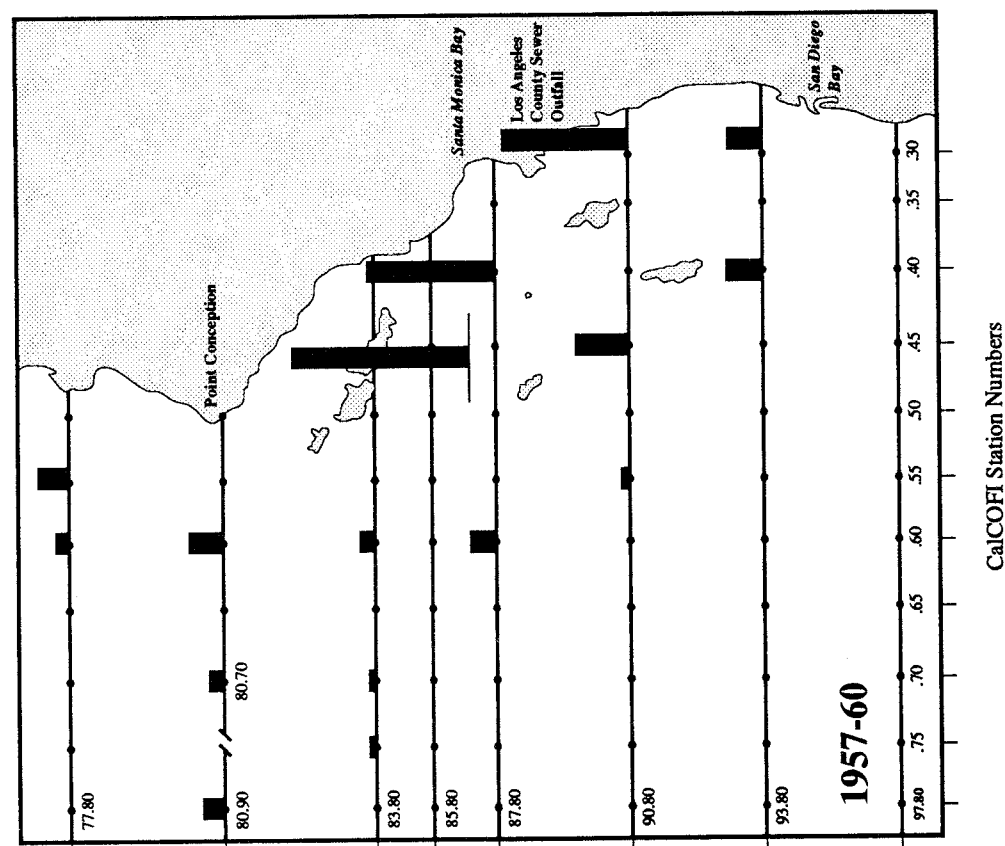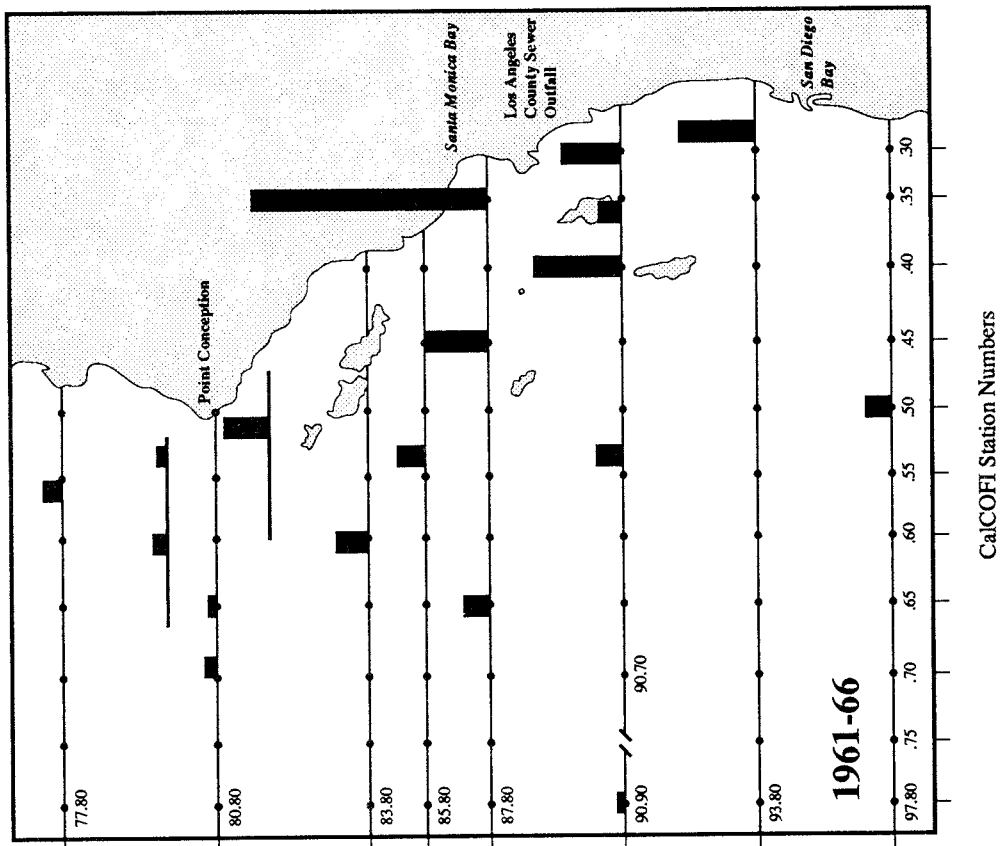Figure 16.20. Levels of tDDT in *S. Leucopsaurus*, 1950-66. Source: MacGregor, 1974.

1961-66

CalCOFI Station Numbers

1957-60
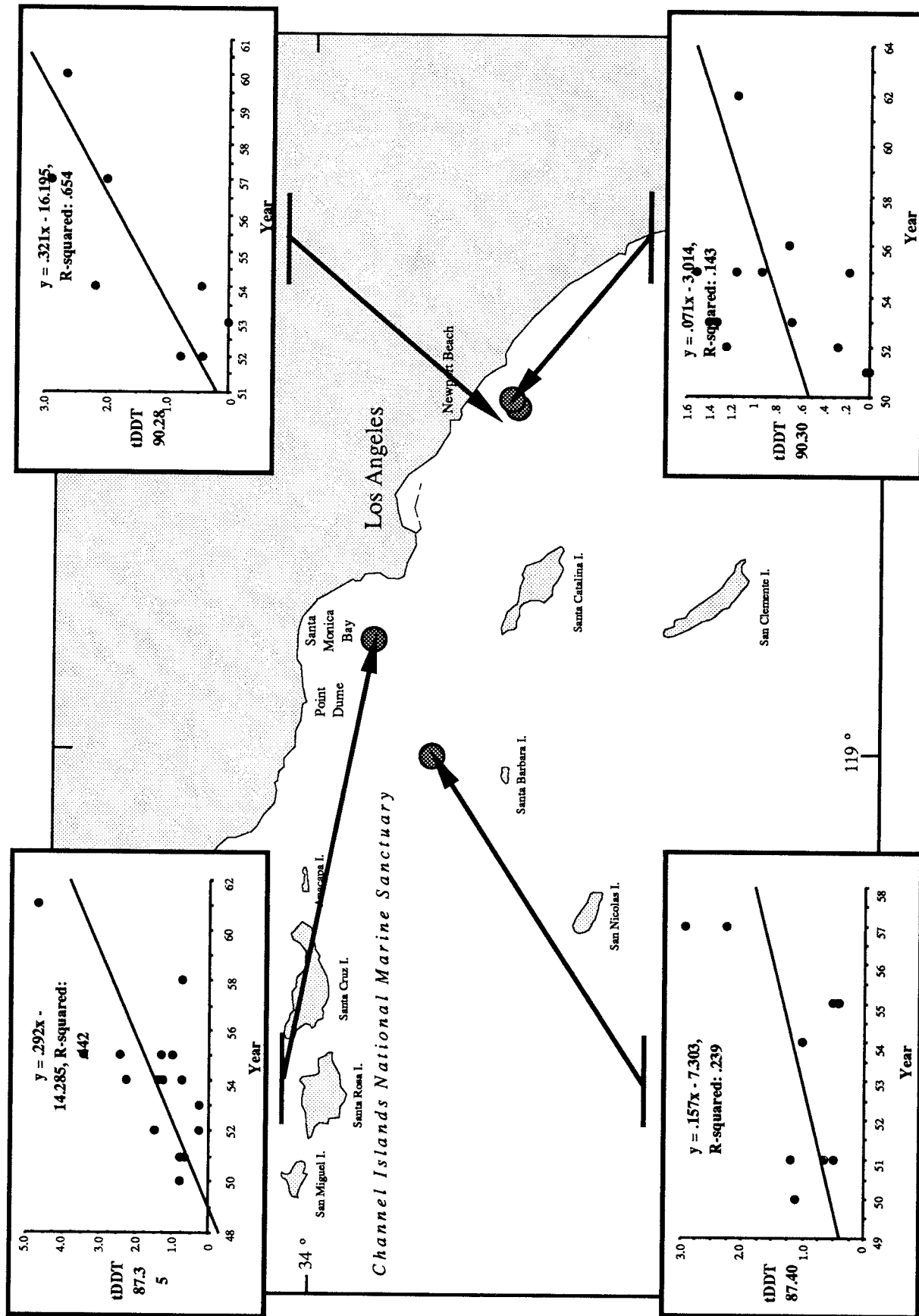
CalCOFI Station Numbers

Figure 16.20 (continued)

Figure 16.21. Selected time series of tDDT measured in specimens of the myctophid fish, Stenobrachius leucopsarus, preserved in museum collections.
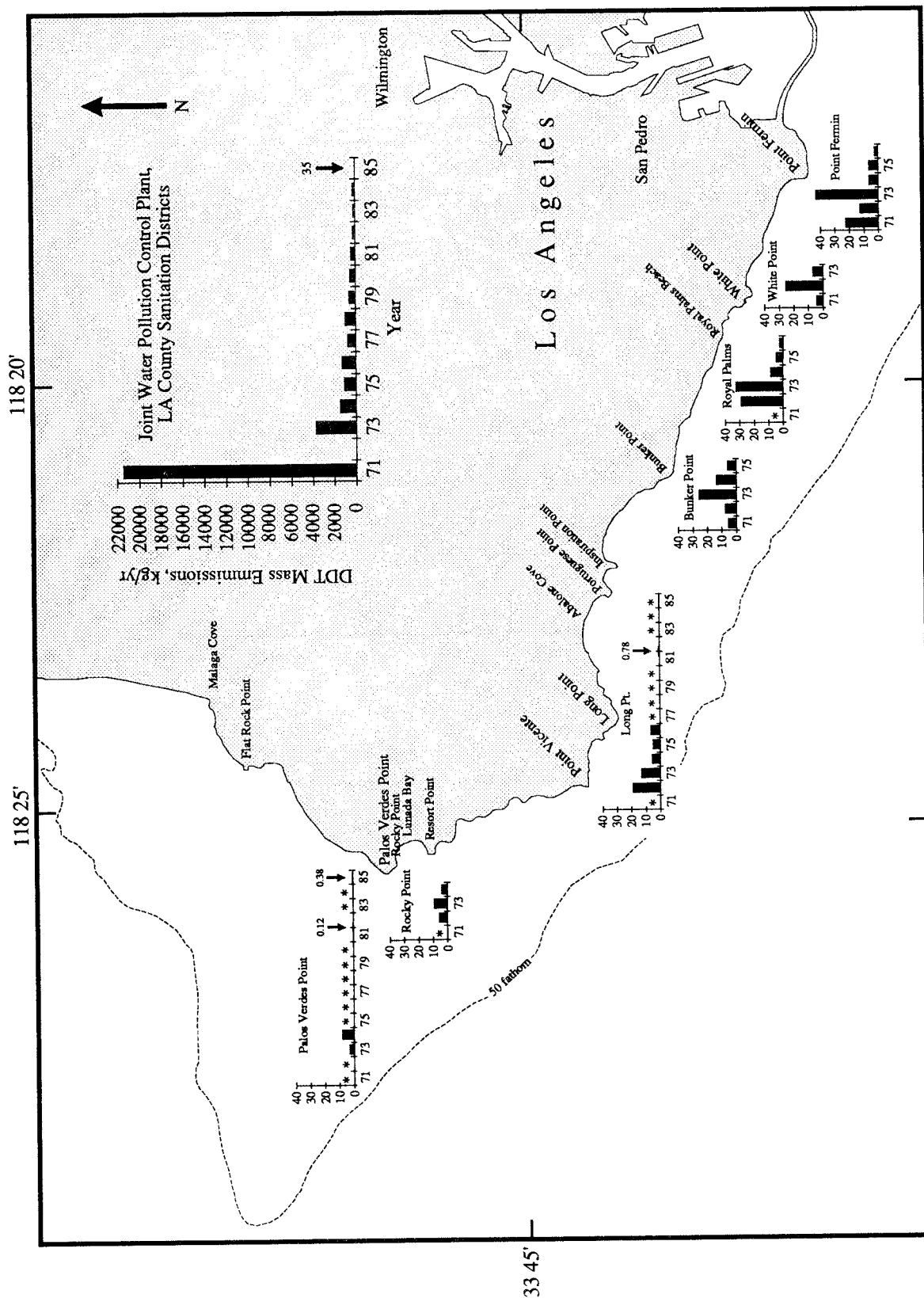Source: MacGregor (1974).

16-36

Figure 16.22. Time series of tDDT in muscle tissue of black perch collected off Palos Verdes Peninsula, 1971-85. Inset: total mass emissions of DDT from JWPCP, 1971-85. Source: SCCWRP, 1987. Source: CSDLAC unpublished data.
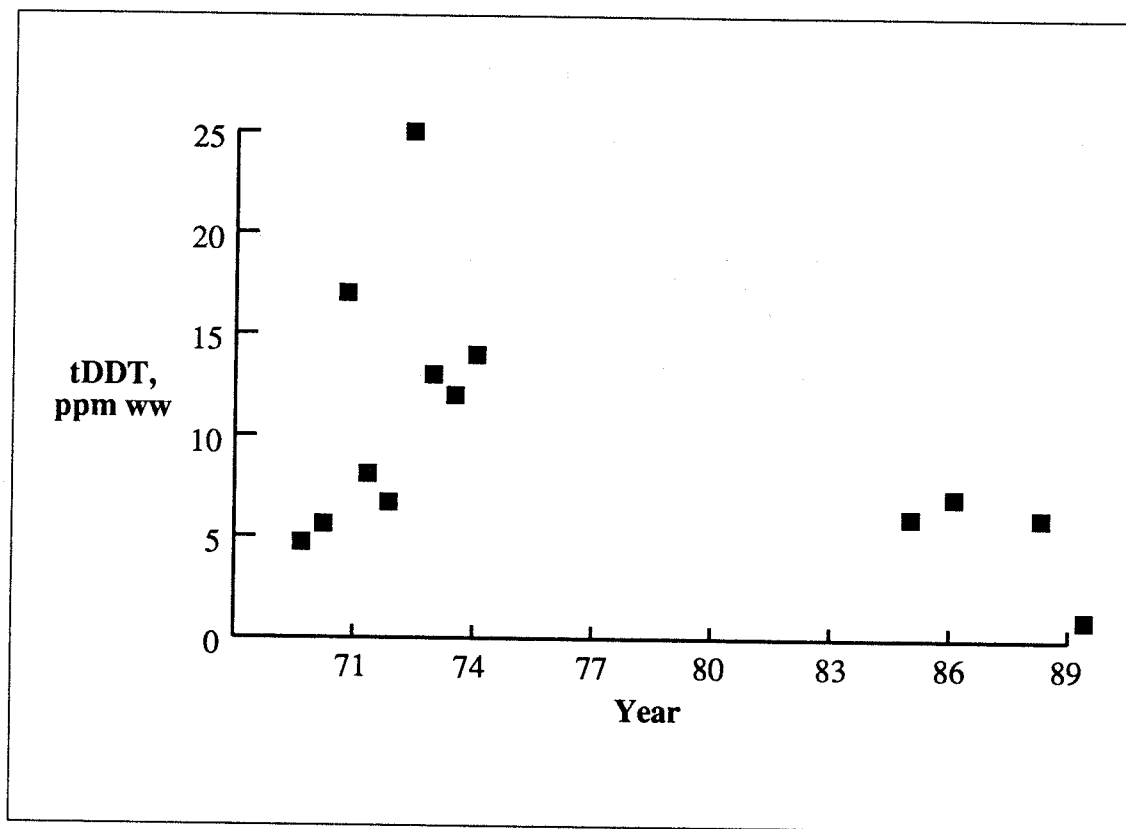
Figure 16.23. Time series of median tDDT in muscle of Dover sole from Palos Verdes 1971-89. Sources: Smokler *et al.*, 1979; CSDLAC, unpublished data.

However, in kelp bass, an analysis of CSDLAC data from the longer period of 1971 to 1988 demonstrates a clearer trend of decreasing muscle tissue concentrations of DDT (Figure 16.24). The CSDLAC results were grouped by location type (*i.e.*, offshore island or mainland), and the nonparametric Mann-Whitney test (Zar, 1984) was employed to test the null hypothesis that there was no difference between the two groups of results. At $\alpha = 0.01$, the null hypothesis was rejected and the mainland and island data sets were analyzed separately.

A nonparametric correlation statistic, Spearman's rank procedure (Zar, 1984) was used to evaluate the correlation of muscle tissue concentrations of DDT with time. Correlations for both site groupings were significant and negative. In the case of the mainland sites, $r_s = -0.406$ at a level of significance less than 0.001. At the island sites, $r_s = -0.620$, with a significance level of 0.002, these results verify a trend of decreasing levels of DDT in kelp bass muscle with time, in areas close to the identified contaminant source and more removed from it.

Analysis of the length of fish sampled over the course of the monitoring program showed that larger fish were selected by researchers in later years. To minimize body burden impacts associated with size, correlation analysis was performed on island and mainland fish that fell within the restricted size range of 29 to 32 cm, a range that was common to both earlier and later years of sampling. Restricting the data sets in this fashion resulted in stronger correlations at mainland sites of $r_s = -0.648$ at a significance level less than 0.001. The resultant sample size for island sites was too limited for meaningful analysis.
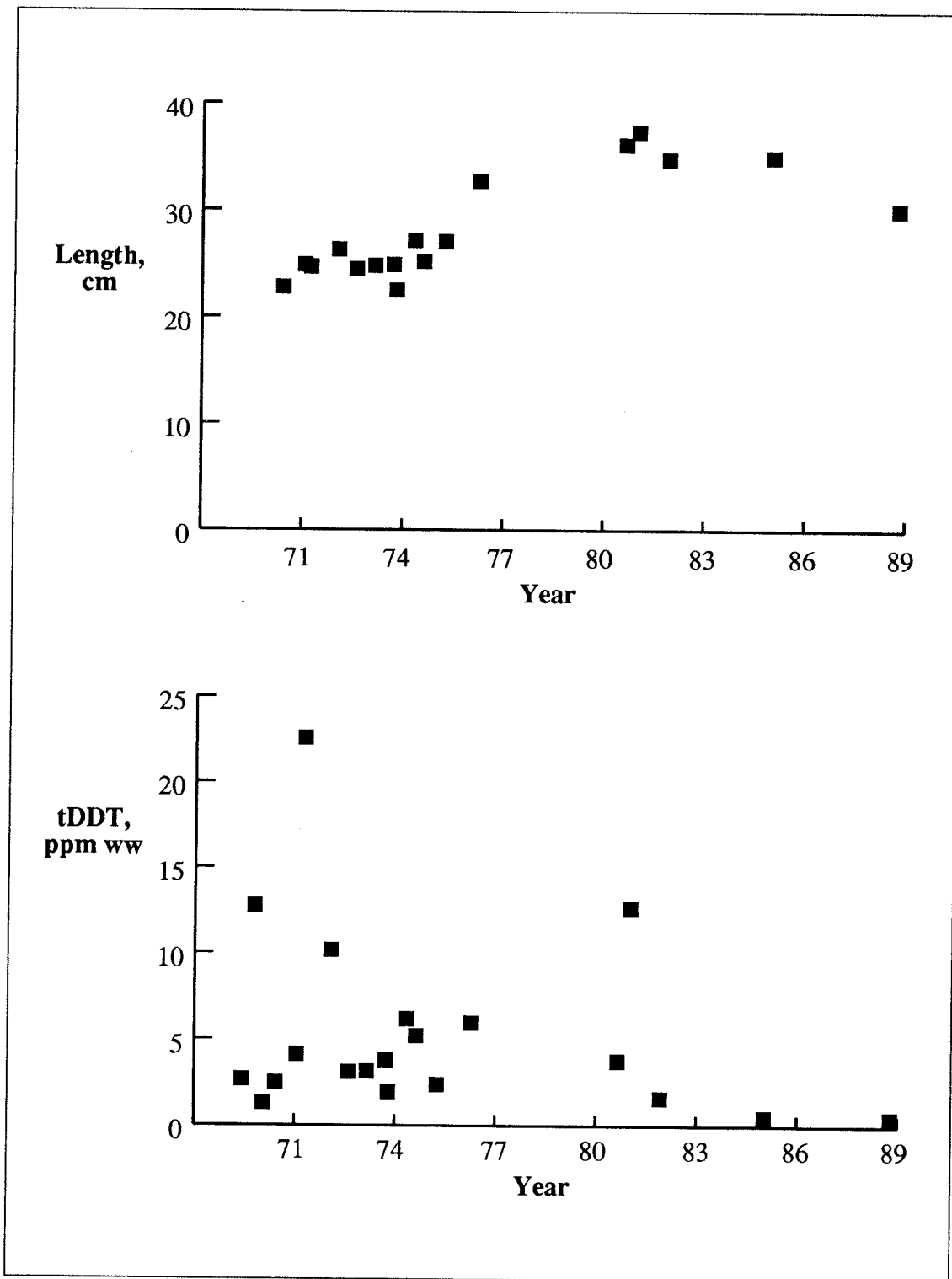
Figure 16.24. Time series of tDDT in muscle and length of kelp bass from Palos
Verdes 1971-88. Source: CSDLAC, unpublished data.

Smokler *et al.* (1979) interpreted DDT muscle tissue concentrations in the context of the percentage that exceeded the U.S. Food and Drug Administration (FDA) guideline of 5.0 ppm ww. For kelp bass collected near the outfall, they found that percentage varied greatly from year to year and from season to season. For example, in spring, 1971, 33 percent of the fish sampled exceeded the guideline, while in the fall of that year, none of the fish did so. In spring and fall of 1976, none of the fish exceeded 5.0 ppm, but in spring of 1977, 40 percent did.

Data from subsequent years are more indicative of downward trends in muscle concentrations of DDT. Isolating discharge zone results from 1981 through 1985 data, shows that in 1981, 5 of the 14 kelp bass sampled (36%) exceeded the FDA guideline; in 1982, 1 of 16 bass (6%) were greater; and in 1985, none of a 20-fish sampled exceeded 5.0 ppm.

Levels of DDT in muscle tissue of white croaker have varied considerably since 1971 (Figure 16.25). Results of analyses of croaker taken from the Palos Verdes peninsula by CSDLAC (unpublished data), SCCWRP (Young et al., 1978, Schafer et al, 1982, and Gossett et al, 1983), and the CDHS (CDHS, 1991) show that, in contrast to results for Dover sole and kelp bass, levels of DDT may not have declined since the early 1980s. This apparent lack of a decline could be due to differences in analytical or sampling methods. It may also be due to recycling of DDT within the food web of white croaker.
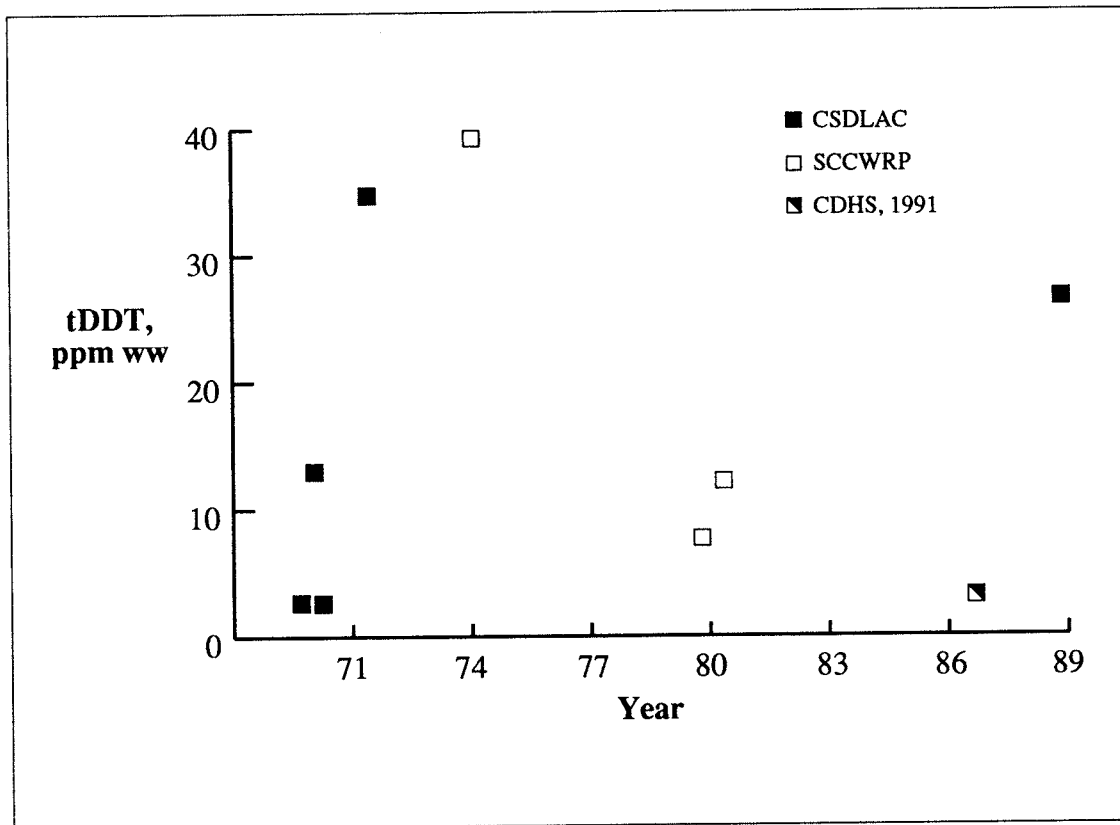

Figure 16.25. Time series of tDDT in muscle of white croaker from Palos Verdes 1971-88. Sources: CSDLAC, unpublished data; SCCWRP, unpublished data; CDHS, 1991.

SUMMARY AND CONCLUSIONS

In bringing together previously collected data on DDT in sediments, mussels, fish, and macroinvertebrates from the Bight, this chapter provided additional temporal, geographic, and taxonomic insight into an already well-described case of heavy DDT contamination in marine life. The data reviewed here indicate DDT has been a contaminant of marine life of the Bight for over 40 years. As in previous reports (Matta *et al.*, 1986; Mearns *et al.*, 1988), a general increase in contamination through the early 1970s was indicated followed by a general decline observable in species both remote from and adjacent to the outfalls that were the primary sources of DDT through the mid-1970s. Recent surveys and additional data not previously reviewed indicate that documentation of future trends in DDT may require careful consideration of species; sampling sites; and size, age, and lipid content of fish.

An unexpected finding was the occurrence of high DDT concentrations in fish collected in 1978 from Upper Newport Bay and in sediment of Bolsa Bay. This area has not been previously suggested as an important source region except in CMW reports. However, sediments collected in 1980 were also relatively high in DDT compared to other harbors and coastal areas. This should not be completely surprising, since Upper Newport Bay drains through an active agriculture area in the Irvine region. CMW and the California Toxic Substances Program identified not only DDT, but toxaphene (a DDT replacement) and dacthal (a pre-emergent herbicide) in bivalves from this area.

The finding of Anderson *et al.* (1982) of technical grade DDT in southern California river mouth sediments collected in 1971 lends further support to the idea that there may have been significant inputs from agriculture areas in the past.

Considering these observations, the recent high levels of DDT in Los Angeles-Long Beach harbors might be expected, especially in view of their proximity to the site of the major production source in Torrance. Somewhat more surprising were the relatively low concentrations of DDT in Marina del Rey and San Diego Harbor. The latter is among the "cleanest" harbors on the coast with respect to DDT, yet it ranks among the more affected by contaminants such as PCBs and copper.

INFORMATION NEEDS

The anomalously high DDT concentrations in Bolsa Bay as reported by Feldmeth (1980) and in Upper Newport Bay bear reexamination. Historically, Bolsa Bay and its adjacent waters drained the formerly productive croplands of Fountain Valley, Westminster, and Garden Grove in Orange County. In 1987, Upper Newport Bay was dredged to re-open channels. The material was disposed of offshore at a dumpsite near and east of the Orange County outfall. The possibility exists that this disposal may have reintroduced an additional load of pesticides, including DDT, into the coastal shelf region. Sediments from this bay should be examined to determine if levels of DDT are still elevated in sediments. Little information exists to confirm that concentrations of DDT in sediments are continuing to decrease in other areas. It would be useful to analyze another sediment core from the Palos Verdes outfall area to determine recent trends in DDT in sediment.

Mussels from Oceanside and Marina del Rey may have shown recent significant increases in DDT concentrations and possible sources should be investigated. Mussels from Corona del Mar should be resampled to determine if increases in DDT seen in the early 1980s are continuing.

NOAA's Ocean Assessment Division has also collected and examined a growing body of data on DDT in bivalves from sites along the northern Baja California coast (Suarez Vidal and Acosta Ruiz, 1976a, b; Sanudo Wilhelmy and Suarez Vidal, 1982; Nishikawa-Kinomora *et al.*, 1988; Gutierrez-Galindo, 1980; Gutierrez-Galindo *et al.*, 1983a; 1984). These data clearly indicate the continuing presence of DDT along the coast of northern Baja California. With additional effort, it should be possible to interpret these Mexican data within the context of U.S. research and monitoring efforts to provide a more cohesive and comprehensive view of marine environmental quality along the Pacific Coast.

While not absolutely necessary to make the case for major reductions in contamination, it would be useful for monitoring agencies to re-sample species, locations, and tissues measured from some of the

earliest collections. These should include many of the commercially important species sampled in 1970 to 1972 by Duke and Wilson (1974) and Stout and Beezhold, as well as some of the harbor and bay species sampled by Butler and Schutzmann (1978) during 1973 to 1976. However, the most compelling history of DDT trends would be produced by analyses of recently collected mid-water fish from CalCOFI program collections thereby extending MacGregor's observations over a 40-year history.

Global sources of DDT may eventually dominate background conditions in the Bight. Sources such as aerial fallout and runoff should be further quantified. It may be useful to repeat and extend the observations of DDT gradients from Mexican waters as uniquely measured in surface dwelling insects (sea skaters, Cheng and Bidleman, 1977).

Many researchers have noted that variability in concentrations of DDT is reduced when values are normalized to TOC in sediments or lipid content in fish and shellfish. Young, Mearns, and Gossett, 1991 have shown that by normalizing sediments p-p'DDE to TOC and Dover sole muscle to its lipid content, the ratio of concentrations in fish muscle to that in sediment from the same area is reduced to approximately 1.7:1. This accumulation factor relationship appears to hold over a wide range of concentrations although was tested with only a small number of samples. It would be useful to test this model with more samples and other benthic species. This model could be useful in predicting levels of contamination in bottom fish when concentrations of DDT in sediment are known.

CHAPTER 17

CHLORDANE AND DIELDRIN

Chlordane (1, 2, 4, 5, 6, 7, 8, 8-octachloro-2, 3, 3a, 4, 7, 7a-hexahydro-4,7-methanoindene), and dieldrin (1, 2, 3, 4, 10, 10-hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-1, 4-endo-exo-5, 8-dimethanonaphthalene) are examples of the organochlorine pesticides called cyclodienes. Cyclodienes are synthetic polycyclic hydrocarbons characterized by two carbon double bonds.

Cyclodiene derivatives exhibit a wide range of toxicological impacts apparently dependent on species, route of exposure, and environmental factors. Like many of the organochlorine pesticides, in acute exposures, cyclodienes affect the central nervous system in insects, animals, and humans (Joy, 1982). Chronic exposure also causes neurotoxicity, and may result in liver damage and growth and reproductive impairment. Although Brooks (1979) stated that no evidence of carcinogenicity existed for either chlordane or dieldrin, later references (Sax, 1981) list both compounds as conclusively carcinogenic in mice and have been identified by the U.S. EPA as tumor-causing agents (U.S. EPA, 1984).

CHLORDANE

Chlordane is a broadly active pesticide used primarily in the control of soil pests. It has been the most important chemical tool for termite control during the past 30 years, and has also been employed to control grasshoppers and cotton pests. It also has been employed as a wood preservative in freight containers. Chlordane was first synthesized in 1944, and its insecticidal properties were described shortly thereafter (as reviewed in Fuchs and Schroder, 1983; Kawano et al., 1988). Chlordane, and other cyclodiene pesticides, were used extensively in agricultural and in domestic applications until evidence mounted that the compounds caused tumors in laboratory animals and were highly persistent in the environment. Due to concerns about human health impacts stemming from applications of the cyclodienes, the U.S. EPA cancelled all uses of the compounds with the exception of subterranean termite control and use on non-food plants in 1974 (Fenske and Sternbach, 1987; U.S. EPA, 1987a; Arruda et al., 1987).

More recently, continuing concerns about chronic exposure resulting from the use of chlordane as a termiticide resulted in further regulatory actions. In late 1987, the Velsicol Chemical Corporation, the sole producer of chlordane in the United States, voluntarily cancelled registration of chlordane pesticides. In accepting that cancellation, the EPA issued an order banning all sales, distribution, and use of the compounds after April 15, 1988 (U.S. EPA, 1987b).

The term "chlordane," as used above, usually refers to "technical chlordane," a complex mixture of more than 45 individual isomers and congeners (Kawano et al., 1988). Included among these are trans- (or alpha) chlordane, cis- (or beta) chlordane, nonachlor (trans- and cis-), and heptachlor. The technical chlordane mix is dominated by trans-nonachlor and trans-chlordane with a small amount of heptachlor and has proved to be more toxic than its individual parent compounds (NRC of Canada, 1974). Oxychlordane is a metabolite of chlordane and nonachlor. In addition, heptachlor alone has been used as a pesticide and is metabolized to heptachlor epoxide in the environment. Monitoring agencies differ in the number of chlordane compounds and metabolites that they measure and report although the most commonly reported are trans-chlordane and trans-nonachlor. Accordingly, uncertainty about exact derivation of an estimate of "chlordane" or "total chlordane" frequently exists and further complicates interpretation of results. Results and studies cited in a recent investigation by Kawano et al. (1988) indicated that chlordane is a global contaminant, being detected in the atmosphere and in fauna of the Antarctic. Kawano et al. (1988) also found that the relative proportions of chlordane constituent compounds varied markedly among organisms emphasizing the critical nature of specifying which chlordane compounds are actually present in samples.

It appears that chlordane inputs to the Southern California Bight have not been measured or estimated. However, computations developed by Summers et al. (1988) suggest that most use and loading of chlordane in southern California occurred in the Los Angeles Basin region, with a peak occurring in 1970 and 1971. Presumably, major sources would be through wastewater discharges and surface run-off. A comprehensive review of the status and history of chlordane contamination in sediments and biota nationwide was completed by Shigenaka (1990).

DIELDRIN

Dieldrin has been employed as an agricultural seed dressing, to protect forest crops, and to control such insects as crickets, cockroaches, mosquitoes, and tsete flies (Fuchs and Schroder, 1983). Chemically, dieldrin is the epoxide of aldrin and is closely related to that compound. Aldrin was first marketed as an insecticide in 1948. While aldrin is rapidly converted to dieldrin in sediments and in biotic systems, dieldrin was synthesized directly in the late 1940s to avoid problems with volatility of aldrin. For these reasons, dieldrin is the dominant compound of the two in the environment and is considered to be the primary toxic metabolite of aldrin. Dieldrin is extremely stable and is one of the most persistent insecticides known (Joy, 1982; Fuchs and Schroder, 1983).

Although aldrin and dieldrin have not been produced in the United States since the mid-1970s, substantial amounts were imported into the country since then. Aldrin accounted for approximately 20 to 25 percent of the U.S. termiticide market prior to 1985. In 1984, the EPA suspended all remaining dieldrin uses, and in 1985, the importation of aldrin and dieldrin was discontinued. In 1987, registration of previous uses was cancelled (U.S. EPA, 1987b).

Young, Heesen, and McDermott (1980b) estimated dieldrin inputs to the Bight. For the period 1972 through 1974, inputs from municipal wastewaters ranged from 95 kg per year in 1974 to less than 200 kg per year in 1972; 10 kg per year entered by way of direct industrial discharges (1973 and 1974). Run-off for 1971 through 1972 was 20 kg and for 1972 through 1973, 65 kg. Thus, while municipal discharges may have dominated inputs in 1971 and 1972, run-off contributions were comparable to wastewater inputs in 1972 and 1973. In 1972 and 1973, the largest amount of dieldrin from wet weather run-off entered from the Los Angeles River (27.9 of 61.6 kg), followed by Ballona Creek (9.66 kg), and Coyote Creek (9.62 kg) that drains into the San Gabriel River.

CHLORDANE AND DIELDRIN IN SEDIMENTS

Neither chlordane nor dieldrin has been routinely measured in sediment samples from offshore areas of the Southern California Bight. However, as a result of investigations by the University of Southern California Harbors Projects, some data do exist for sediments in Marina del Rey (Soule and Oguri, 1985; 1986; 1987) and in Los Angeles-Long Beach harbors (Chen and Lu, 1974; Soule and Oguri, 1980a).

The concentration of chlordane has been higher in Marina del Rey than in Los Angeles-Long Beach harbors (Table 17.1). Concentrations in three annual surveys in Marina del Rey ranged from below detection limits (0.001 ppm dw) to 0.721 ppm dw. Mean survey concentrations ranged from 0.055 ppm dw in 1985 to 0.183 ppm dw in 1984. By contrast, concentrations in Los Angeles-Long Beach harbors' sediments averaged 0.008 ppm with a range of below detection limits (0.01 ppm dw) to 0.040 ppm dw. It has not been possible to determine if these data refer to "chlordane" as a total of several, or of all compounds of technical chlordane. Until that question is answered, these results should not be compared to other data sets.

Table 17.1. Mean, median, minimum, and maximum chlordane concentrations in surface sediment from selected surveys, 1973 through 1985 in ppm dw.

Site	Year	N	Mean	Median	Min	Max	SD	Source
Bays and Harbors:								
Marina del Rey	1984	12	0.183	0.070	0.001	0.721	0.234	1
	1985	12	0.055	<0.005	<0.005	0.335	0.123	2
	1987	13	0.064	0.025	0.001	0.270	0.086	3
Los Angeles-Long Beach harbors	1978	31	<.01	<0.01	<0.01	0.04	0.01	4
OVERALL		68	0.008		0.001	0.721		

1 Soule and Oguri, 1985	3 Soule and Oguri, 1987
2 Soule and Oguri, 1986	4 Soule and Oguri, 1978

Dieldrin was less frequently detected in harbors (Table 17.2). Concentrations in Marina del Rey ranged from less than 0.002 to 0.013 ppm dw and may have been slightly less than levels in Los Angeles-Long Beach harbors (0.001 to 0.061 ppm dw).

Table 17.2. Mean, median, minimum, and maximum dieldrin concentrations in surface sediment from selected surveys, 1973 through 1987 in ppm dw.

Site	Year	N	Mean	Median	Min	Max	SD	Source
Bays and Harbors:								
Marina del Rey	1984	12	0.002	0.002	0.002	0.003	0.0005	1
	1985	12	0.003	0.002	0.002	0.011	0.003	2
	1987	13	0.003	0.001	<0.0002	0.013	0.004	3
Los Angeles-Long Beach harbors	1973	31	0.007	0.010	0.001	0.061	0.014	4
	1978	31	<0.002					5
OVERALL		99			0.001	0.061		

1 Soule and Oguri, 1985	4 Chen and Lu, 1974,
2 Soule and Oguri, 1986	5 Soule and Oguri, 1978
3 Soule and Oguri, 1987	

In the NOAA NS&T 1984 and 1985 Benthic Surveillance surveys and the 1986 Mussel Watch surveys, sediments were analyzed for trans-chlordane, trans-nonachlor, heptachlor, heptachlor epoxide, dieldrin, and aldrin. Total chlordane (defined as the sum of trans-chlordane and trans-nonachlor) ranged from below detection limits at most coastal sites to 0.011 ppm dw at Long Beach in 1985, 0.0097 ppm off Royal Palms (Palos Verdes, 1986), and 0.005 and 0.008 ppm dw at a site in San Diego Harbor in 1984 and 1985, respectively (Figure 17.1). In the 1984 and 1985 Benthic Surveillance surveys, all concentrations of dieldrin were below detection limits with the exception of one sample near Long Beach (0.003 ppm dw). Likewise, all dieldrin measurements were below detection limits in the 1986 Mussel Watch with the exception of one sample at Cabrillo Beach in Los Angeles Harbor (0.008 ppm dw), three samples offshore from Marina del Rey (0.00037 to 0.0006 ppm dw), and two sites off Oceanside (0.00037 and 0.00039 ppm dw; data not shown graphically).

Overall mean levels of chlordane and dieldrin in sediments sampled nationwide by NOAA's NS&T Program between 1984 and 1989 have been very low. The overall mean level of chlordane was 0.0014 ppm dw (median, 0.004 ppm dw). The overall mean level of dieldrin was 0.0009 ppm dw (median, 0.0002 ppm dw).

Based on a limited number of previous studies that associated sediment chemistry with biological effects, Long and Morgan (1990) estimated concentrations of dieldrin and chlordane that are often associated with toxic effects. The range of concentrations of dieldrin that cause effects (ER-L to ER-M) was estimated to be 0.00002 to 0.008 ppm dw. For chlordane the range (ER-L to ER-M) was 0.0005 to 0.006. These lower concentrations have been exceeded in sediment from Marina del Rey and Los Angeles-Long Beach harbors.

In summary, although there have been relatively few direct measures of chlordane and dieldrin in sediments of the Bight, it would appear that Marina del Rey sediments contained higher concentrations of chlordane and lower concentrations of dieldrin than did those of Los Angeles-Long Beach harbors.
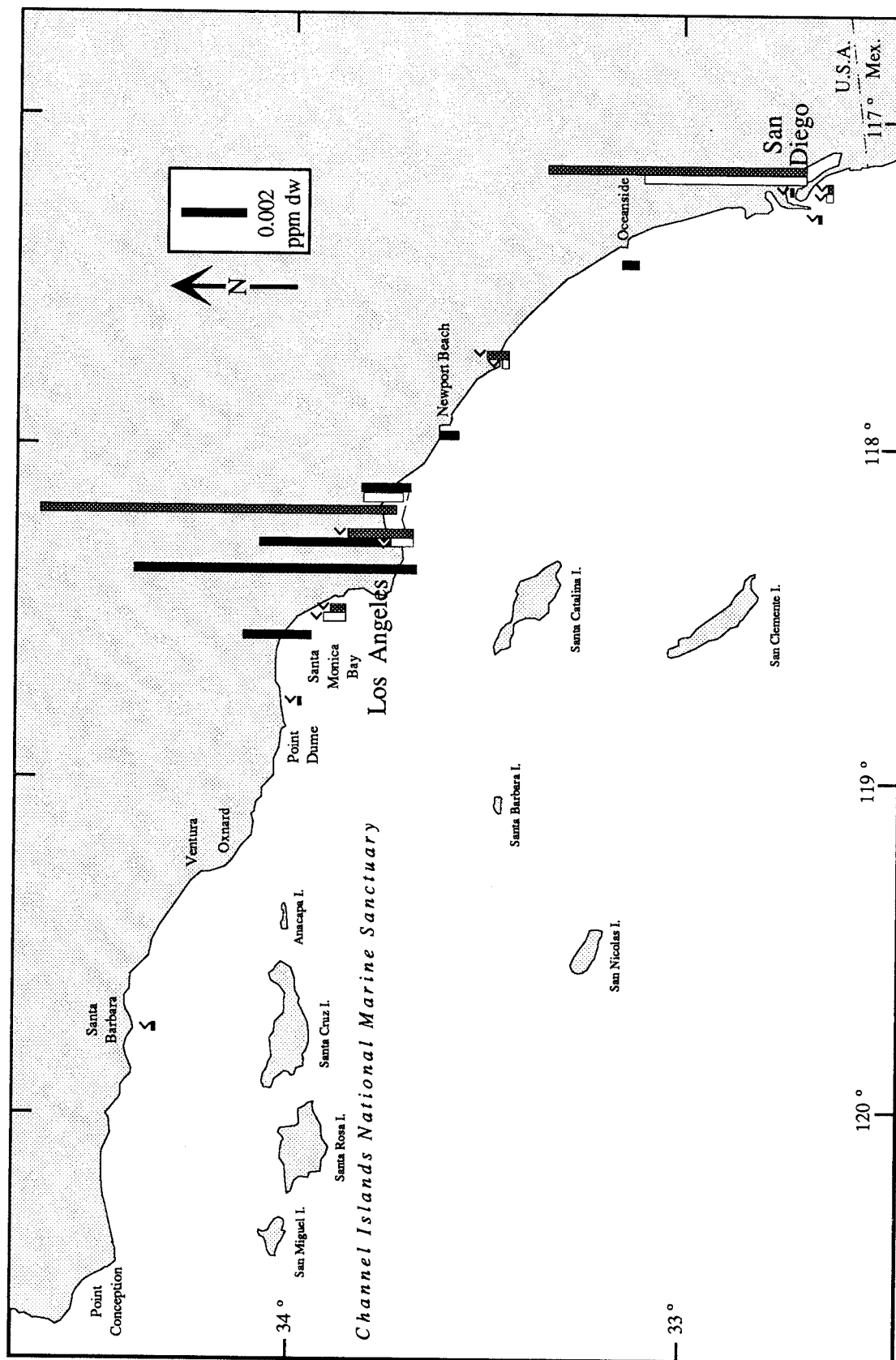
Figure 17.1. Median chlordane concentrations in the surficial sediments of the Southern California Bight based on data from NOAA's NS&T Program Benthic Surveillance Project for 1984 (▯) and 1985 (▦) and Mussel Watch Project for 1986 (▮) (NOAA, 1988 and unpublished data). The bars with a < represent the median detection limits at sites where concentrations were below those limits.

CHLORDANE AND DIELDRIN IN MUSSELS

Between 1967 and 1977, the NPMP collected and analyzed *M. edulis* mussels from three sites in the Southern California Bight (Hedionda Lagoon, Anaheim Slough, and Point Mugu Lagoon) for concentrations of dieldrin and chlordane (Butler, 1973; Butler *et al.*, 1978). Grouped results from this sampling and analysis are summarized in Table 17.3. All 52 measurements for chlordane were less than the detection limit of 0.01 ppm ww. Out of 52 samples, 29 contained less than 0.01 ppm of dieldrin.

Table 17.3. Summary of grouped results from analyses of *M. edulis* sampled 1967 through 1977 by the NPMP (Butler, 1973; Butler *et al.*, 1978).

Site	Total Samples Analyzed	Pesticide	N <0.01 ppm*	0.05<N<0.10 ppm*	N ≥ 0.10 ppm*
Hedionda Lagoon	9				
		Dieldrin	5	4	0
		Chlordane		9	0
Anaheim	21				
		Dieldrin	11	8	2
		Chlordane	0	0	
Point Mugu	22				
		Dieldrin	13	8	1
		Chlordane	22	0	0

* N = number of samples analyzed

With most measurements at or near analytical detection limits, no clear trend in the NPMP data was apparent. The regulatory history of the cyclodienes (most uses were discontinued in 1974) was reflected only to the extent that all concentrations measured in 1977 (the only sampling conducted by this particular program after the EPA action) were below detection limits (less than 0.01 ppm ww).

In January and February of 1982, the CMW Program collected and analyzed *M. edulis* and *M. californianus* from eight sites in the Southern California Bight for concentrations of dieldrin and chlordane. These results, illustrated in Figures 17.2 and 17.3, show that highest mussel tissue concentrations for both compounds were found in Colorado Lagoon, a small saltwater lagoon connected to Alamitos Bay (near Long Beach) that receives limited tidal circulation and flushing. The concentrations of 1.53 ppm dw chlordane and 0.07 ppm dw dieldrin exceeded concentrations at Marina del Rey, the next most contaminated site, by factors of about three. Hayes and Phillips (1986) observed that inflow to Colorado Lagoon is primarily stormwater run-off and, because of minimal flushing, pollutants are likely to remain in the lagoon and build to higher levels than in other areas.

The relatively low levels of cyclodiene compounds measured at the Royal Palms site (0.032 ppm dw chlordane, 0.006 ppm dieldrin) suggest that inputs from municipal discharges were a less significant source of contamination than they were for other chlorinated compounds such as PCBs or DDT (see chapters 15 and 16). This is consistent with the regulatory record for cyclodienes. Restrictions on manufacturing and general use of the materials would imply that only limited amounts of residues would be channeled into waste treatment plants. However, continued use of chlordane, aldrin, and dieldrin as termiticides would continue to contribute to stormwater run-off. Arruda *et al.* (1987) determined that elevated concentrations of chlordane in freshwater fish tissue corresponded to greater degree of urbanization. They specified urban and suburban use of the compound as a termiticide as a likely source for tissue residues.
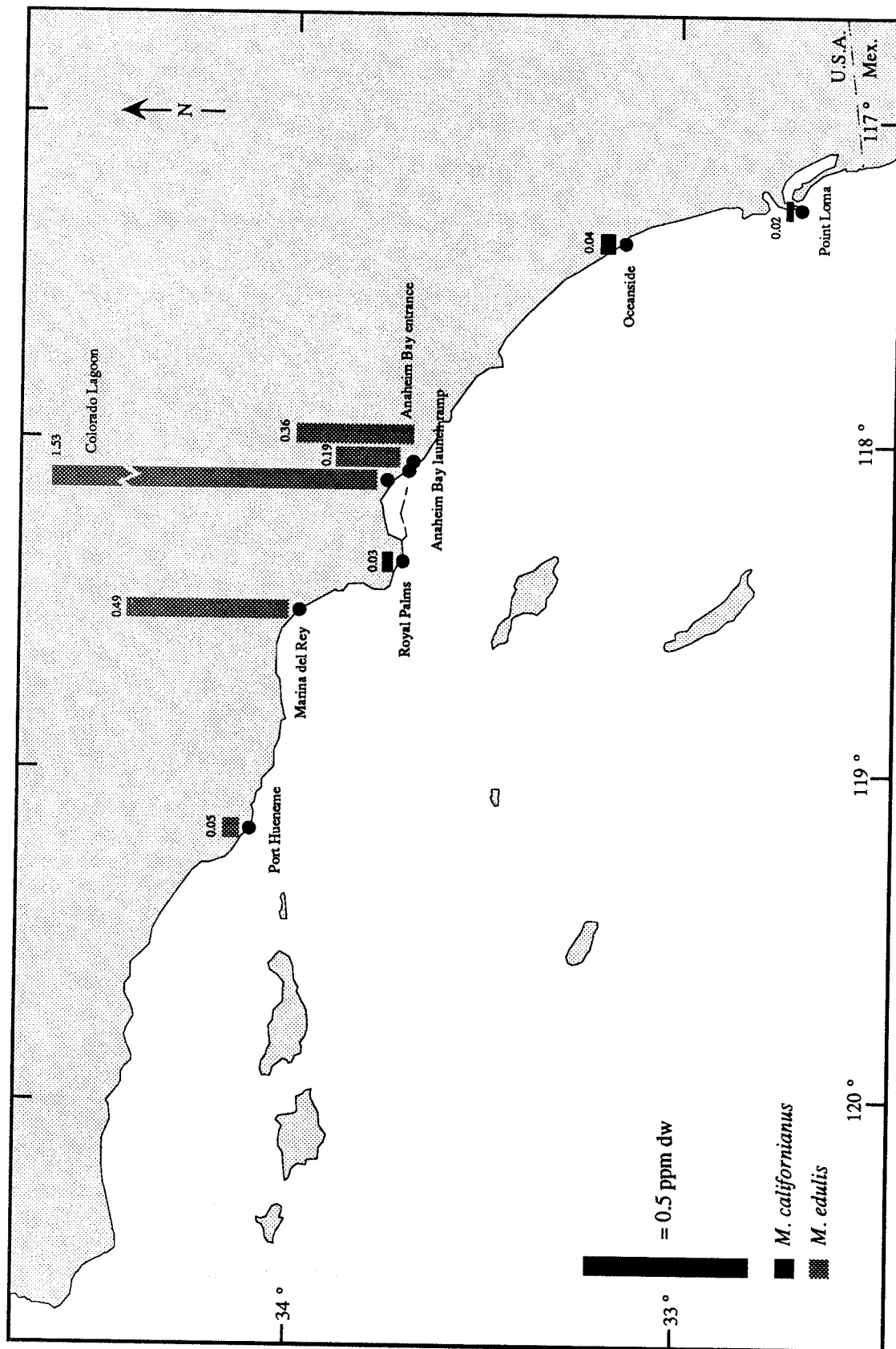
Figure 17.2. Chlordane in soft body tissue of whole mussels sampled in the Southern California Bight in January and February 1982. Source: Phillips, 1988.
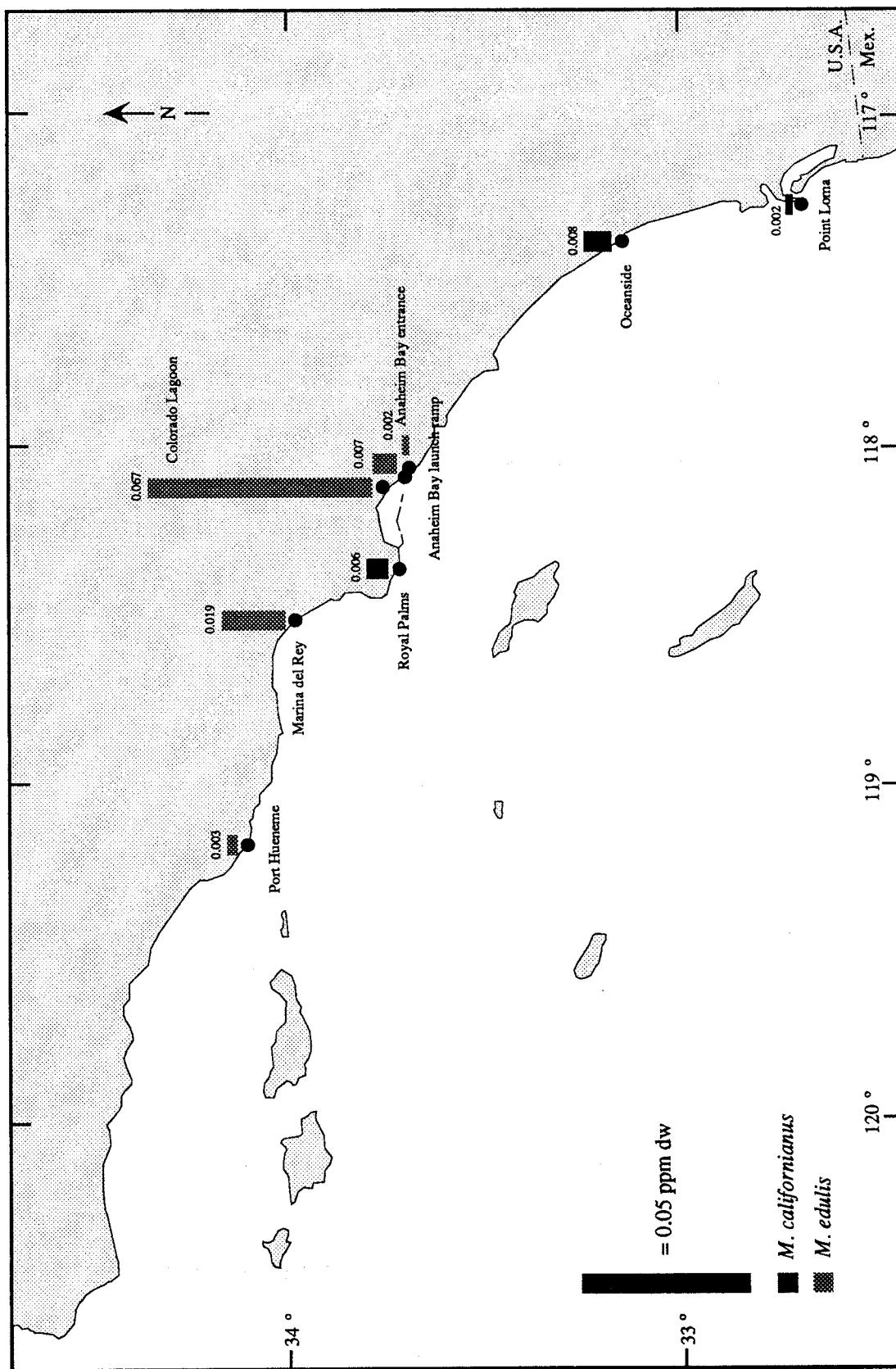
Figure 17.3. Dieldrin in soft body tissue of whole mussels sampled in the Southern California Bight in January and February 1982. Source: Phillips, 1988.

As discussed previously, higher concentrations found in resident mussels of Colorado Lagoon may reflect such nonpoint source inputs. Marina del Rey, an enclosed harbor area with limited circulation and large inputs from stormwater run-off by way of Ballona Creek, also showed elevated *M. edulis* tissue levels of chlordane and dieldrin (0.5 and 0.02 ppm dw, respectively) as compared to other sites sampled in 1982.

The NS&T Program Mussel Watch Project sampled and analyzed chlordane and dieldrin in *M. edulis* and *M. californianus* at 16 Southern California Bight sites in 1986. Results, shown in Figures 17.4 and 17.5, generally affirmed regional trends observed in 1982 CMW Program measurements. Elevated cyclodiene concentrations in mussel tissue were found in harbor/marina areas with large run-off inputs and restricted flushing. Highest concentrations of chlordane for southern California sites were found in Marina del Rey, where tissue concentrations in *M. edulis* measured 0.06 ppm dw; and in Anaheim Bay, with levels in *M. californianus* also at 0.06 ppm. Results for dieldrin were similar, maximum levels in southern California occurred in Anaheim Bay (0.03 ppm) and the next highest in Marina del Rey (0.01 ppm). Possible sources to Marina del Rey have been mentioned previously. At Anaheim, Hayes and Phillips (1986) noted that several potential sources of compounds such as cyclodienes exist in the Anaheim Bay watershed, among them two large flood control channels. It would appear that nonpoint sources of chlordane and dieldrin are of relatively greater importance in determining distributions of mussel concentrations in the Southern California Bight than is the case for many other contaminants.

Overall mean levels of chlordane in mussels sampled nationwide by NOAA's NS&T Program between 1986 and 1989 were 0.031 ppm dw for *M. edulis* and 0.015 ppm dw for *M. californianus*. Median values were lower: 0.019 ppm dw in *M. edulis* and 0.009 ppm dw in *M. californianus*, median dieldrin values were 0.005 ppm dw (*M. edulis*) and 0.007 ppm dw (*M. californianus*).

Time series of chlordane and dieldrin concentrations in southern California mussels sampled in the CMW Program are shown in Figures 17.6 and 17.7. The long-term reference sites at Royal Palms and Oceanside offer the most opportunity to assess temporal trends of cyclodiene body burdens. However, no clear trends are evident for chlordane. Dieldrin results suggest a peak in concentrations in 1983, with declines in subsequent years. Analyses of Colorado Lagoon mussels in 1982 and 1985 may indicate a decline in concentrations of both chlordane and dieldrin, although the minimum concentrations measured there in late 1985 (approximately 0.5 and 0.03 ppm dw for chlordane and dieldrin, respectively) remain among the highest measured in the Southern California Bight by the CMW Program.

Risebrough (1987) measured concentrations of six chlordane compounds in resident *M. californianus* collected in the Bight between 1971 and 1986. However, not all compounds were analyzed at all sites or in all years, which prevents the broad evaluation of temporal trends.

Trans-chlordane was measured more often by Risebrough (1987) than any of the other four chlordane-family compounds, and provided a relative basis for comparison among all sites and all years sampled in the study. By far, the highest concentrations of trans-chlordane measured in resident mussels occurred at Santa Monica Pier (0.065 ppm dw in June 1971) and at Royal Palms (0.024 ppm and 0.27 ppm dw in July and November 1971, respectively). The 1985 measurement at Santa Monica (0.002 ppm) and the 1986 value at Royal Palms (0.003 ppm) indicated trans-chlordane decrease of an order of magnitude from 1971 levels; yet these recent measurements were still greater than or equal to the highest of the concentrations at island sites, even those from the early 1970s, when higher levels were encountered throughout the Southern California Bight.

Risebrough's (1987) results for three sites--Royal Palms, Santa Barbara Island, and Santa Monica Pier-- are shown in Figure 17.8. At all three sites, the limited number of data points suggests steady declines in concentrations of chlordane-family compounds with time. If these data are representative of downward temporal trends in resident mussel tissue chlordane concentrations, this would stand in contrast to CMW results, in which few sites showed discernible temporal trends. It would however, be consistent with the regulatory history of chlordane, as was previously discussed.

NOAA's NS&T Program detected no significant trend in total chlordane or dieldrin levels in mussels sampled between 1986 and 1988 (NOAA, 1989).
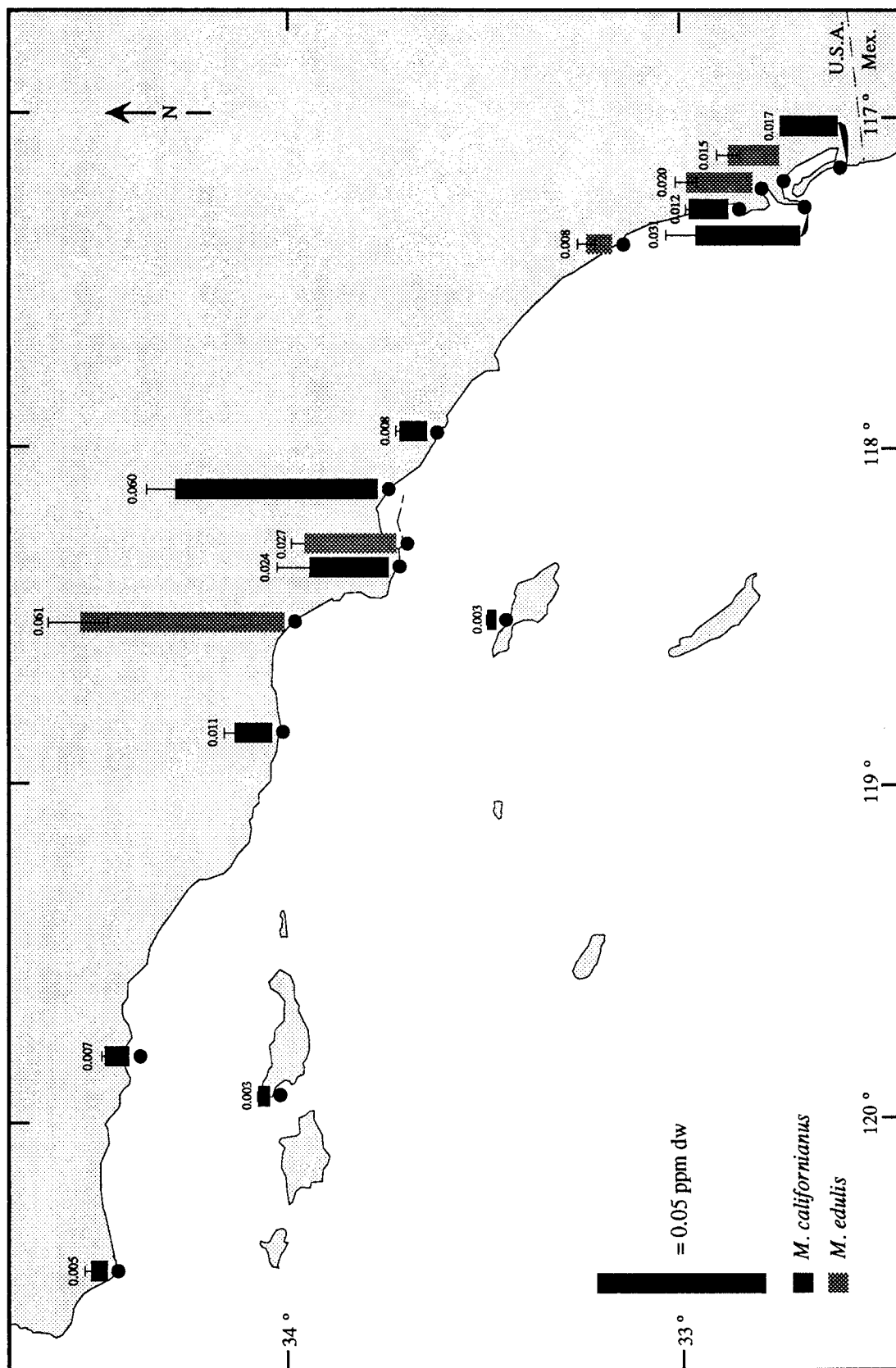
Figure 17.4. Chlordane in soft body tissue of whole mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.
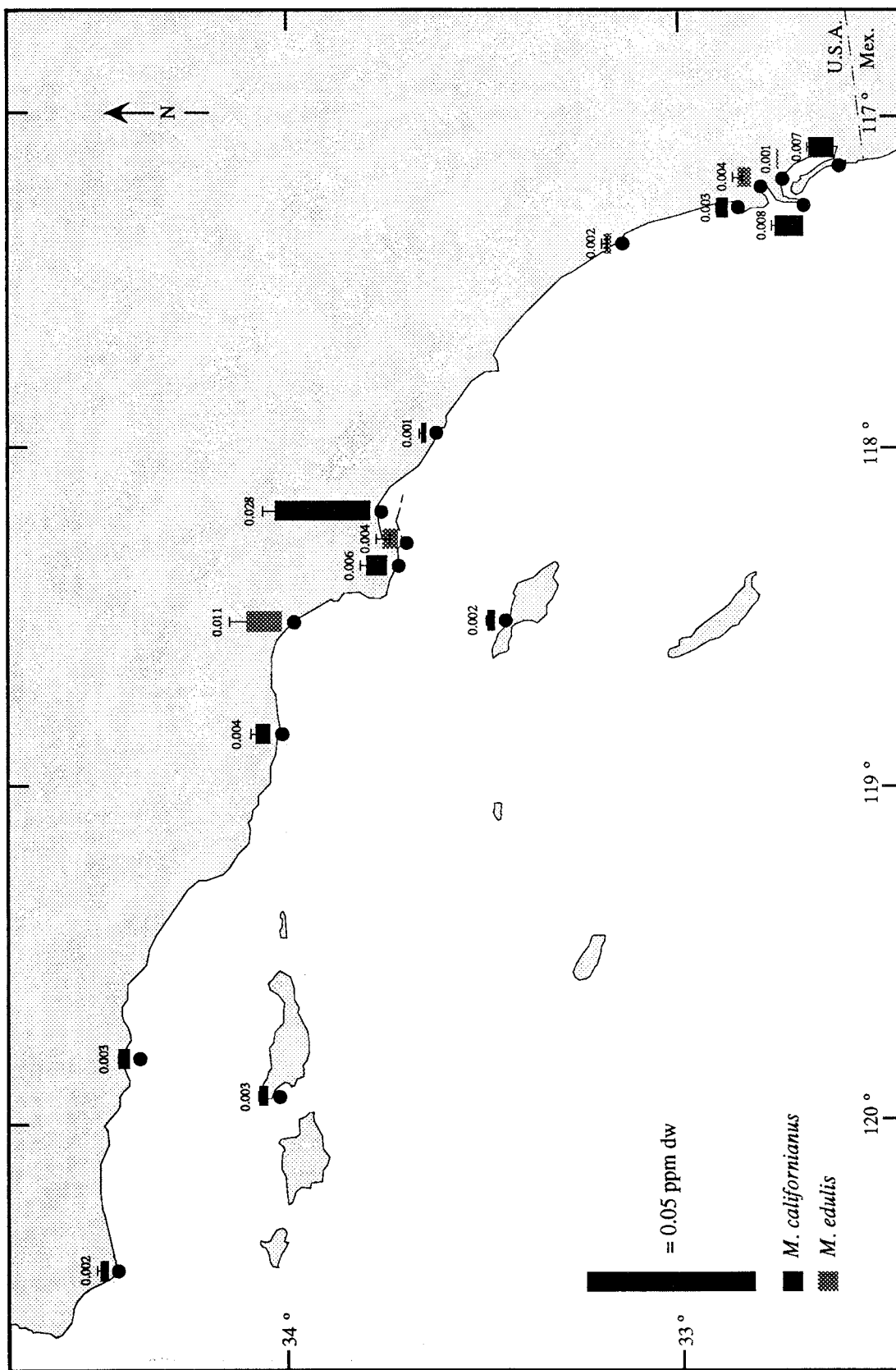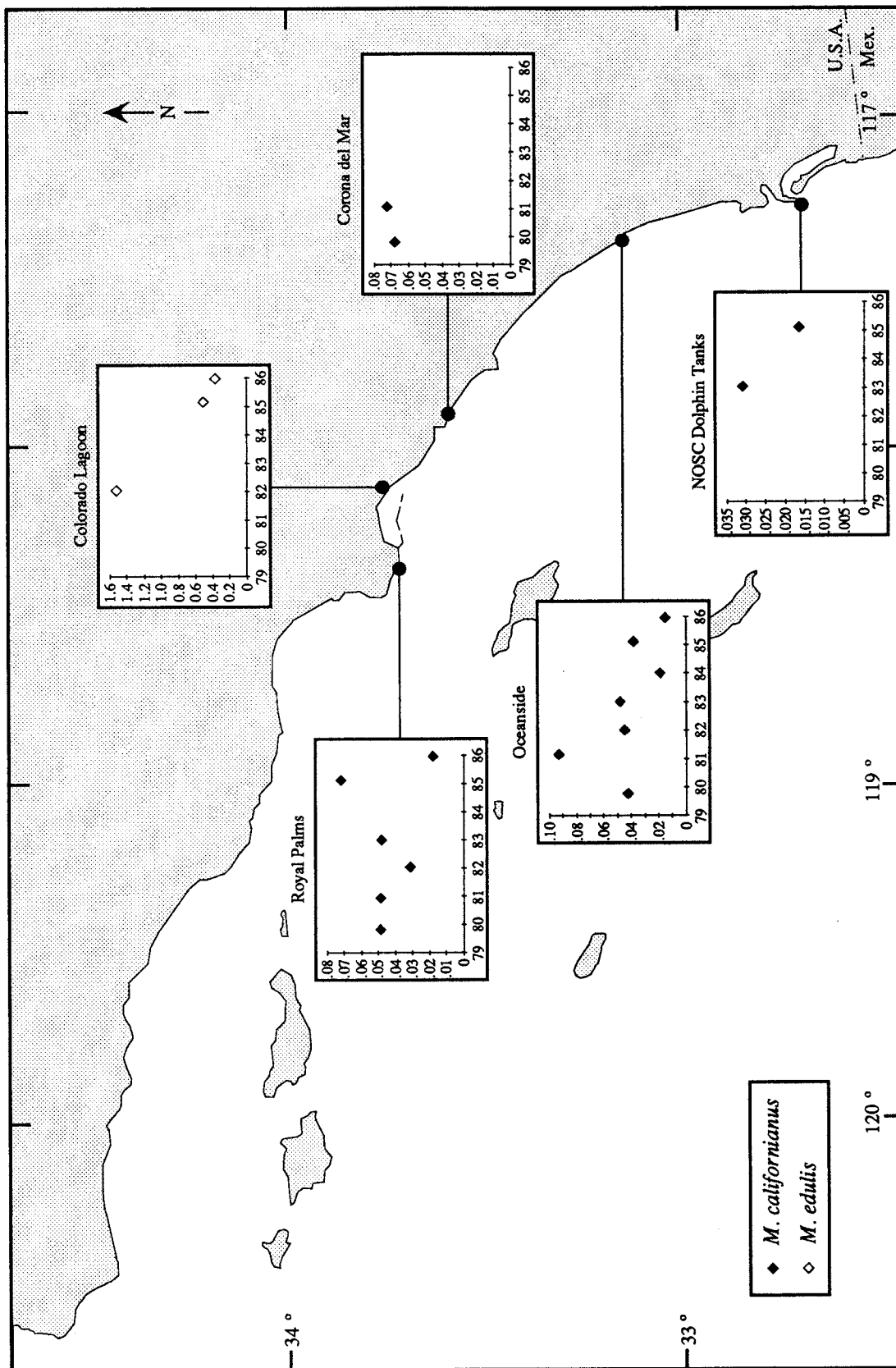
17-9

Figure 17.5. Dieldrin in soft body tissue of whole mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA, 1989.

17-10

Figure 17.6. Time series of chlordane in soft body tissue of whole mussels sampled in the Southern California Bight, 1979-85. Note scale differences among data plots. Source: Phillips, 1988.
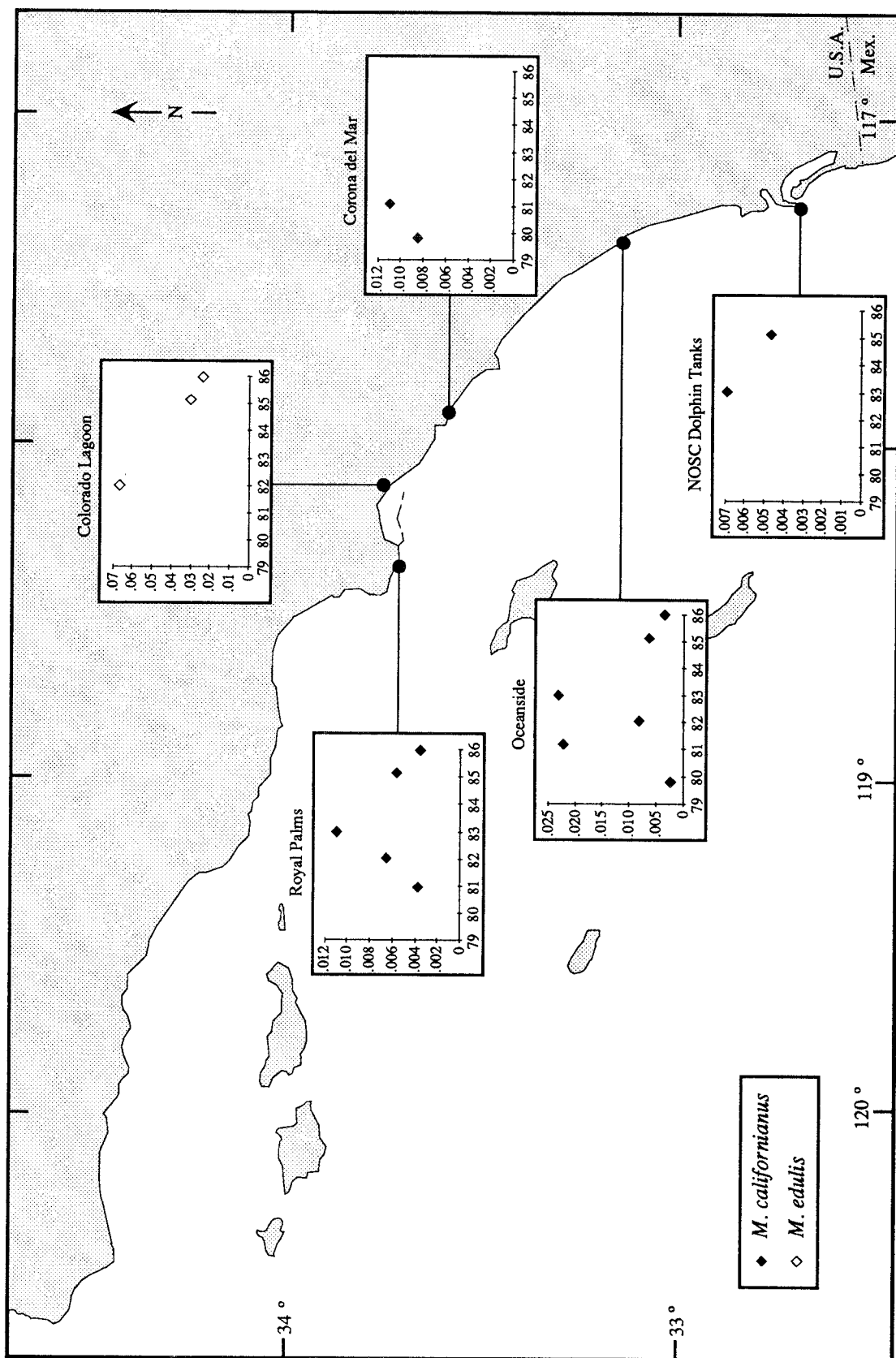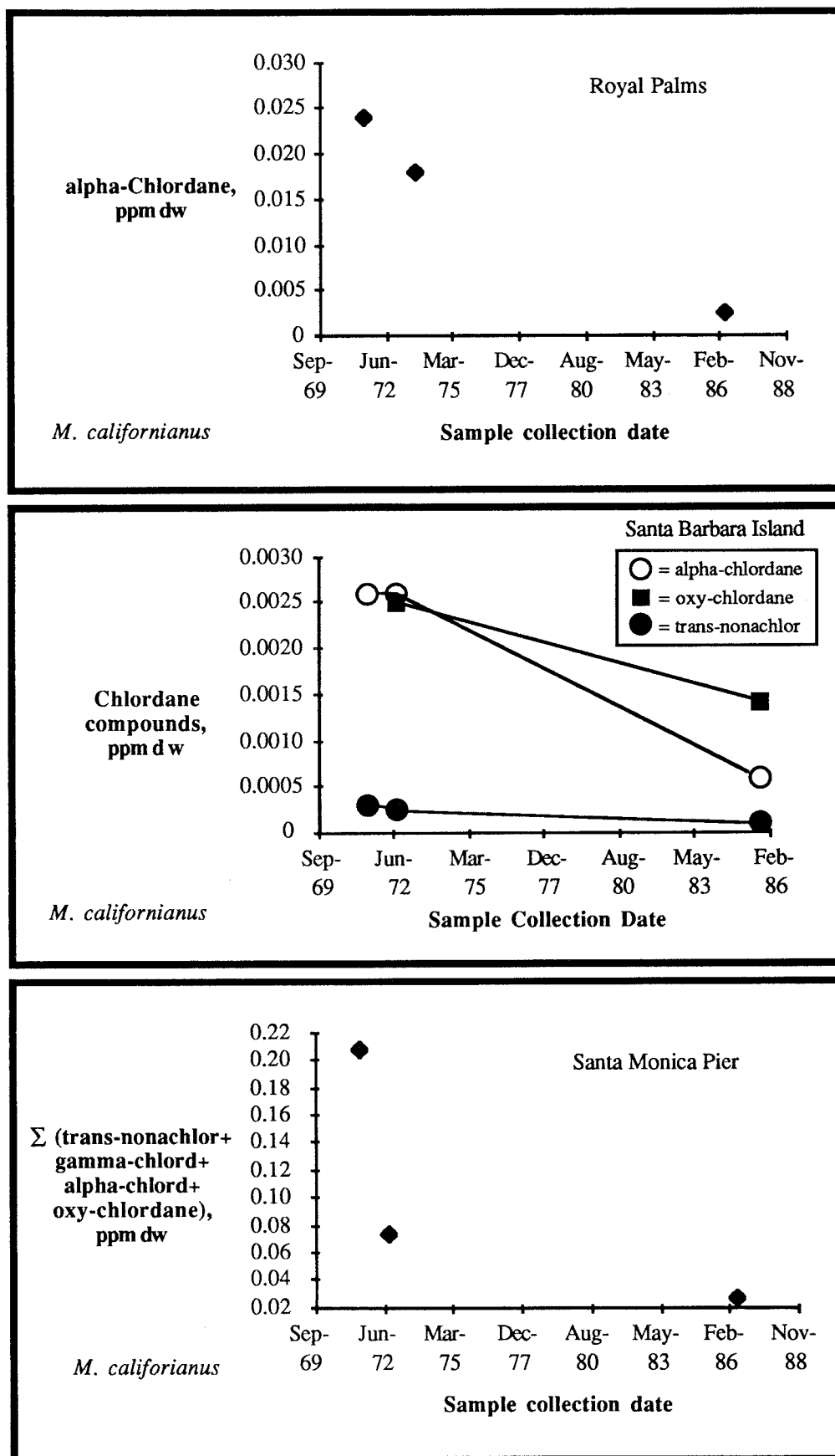
Figure 17.7. Time series of dieldrin in soft body tissue of whole mussels sampled in the Southern California Bight, 1979-85. Note scale differences among data plots. Source: Phillips, 1988.

Figure 17.8. Chlordane compound concentrations in resident mussels collected in the Southern California Bight 1971-86. Source: Risebrough, 1987.

CHLORDANE AND DIELDRIN IN FISH AND OTHER SPECIES

Chlordane and dieldrin have been sporadically measured in fish and macroinvertebrates from the Bight since 1971. However, analyses have not been sufficiently described to identify comparable historical data sets. Neither compound was apparently included in past SCCWRP surveys.

Chlordane and dieldrin have been measured in fish and macroinvertebrates during monitoring surveys off Huntington Beach since 1974 by the CSDOC, and off Palos Verdes between 1971 and 1975 by the CSDLAC. None of these compounds were detected above prevailing detection limits in several hundred fish and macroinvertebrate samples at the CSDOC sites. However, both chlordane and dieldrin were detected in CSDLAC sampling. Muscle of several specimens of three species of fish collected from the Palos Verdes peninsula between 1971 and 1975 yielded tentatively identified heptachlor concentrations ranging from 0.12 to 0.17 ppm ww. In addition, 37 specimens of several species had tentatively identified heptachlor epoxide concentrations above 0.1 ppm ww; the highest was 0.59 ppm ww in muscle of a Dover sole collected in 1975 from a depth of 60 meters near the CSDLAC outfall (CSDLAC, unpublished data). Two rockfish from Palos Verdes collected during that period contained about 0.7 ppm ww of dieldrin (CSDLAC, unpublished data).

In a 1985 survey, the LARWQCB included total chlordane in a survey of contaminants of kelp bass and other organisms from nine coastal and island sites. Concentrations in muscle of kelp bass ranged over an order of magnitude, from 0.002 ppm ww at Santa Barbara Island, to 0.019 ppm ww at Whites Point on the Palos Verdes Peninsula (Risebrough, 1987; Figure 17.9). Concentrations in liver ranged over a slightly greater range, from 0.017 ppm ww at the southeast end of Santa Catalina Island to 0.386 ppm ww at Whites Point (Figure 17.9). As seen in Figure 17.9, these data suggest the existence of a gradient of increasing total chlordane contamination of fish with increasing proximity to the Palos Verdes area.

Data on levels of total chlordane (trans–chlordane plus trans-nonachlor) from the 1984 and 1985 NOAA NS&T Benthic Surveillance surveys provide further evidence for this possible chlordane gradient. Concentrations were comparable in range to those reported by Risebrough (1987). In livers of hornyhead turbot from five sites, total chlordane concentrations ranged from about 0.05 ppm ww at two southern sites (Dana Point and San Diego Bay) to about 0.3 ppm ww in one composite collected at a site near Seal Beach at the east end of Long Beach Harbor (Figure 17.10). Intermediate concentrations (0.13 to 0.15 ppm ww) occurred in fish from San Pedro Canyon (offshore from Los Angeles Harbor) and at a shallow-water site in Santa Monica Bay. Higher concentrations were also found in white croaker from the Seal Beach site (0.53 ppm ww) than the Dana Point reference site (about 0.05 ppm ww). Barred sand bass from San Diego Harbor (0.35 ppm ww) contained higher levels of total chlordane than the same species from the reference site (0.08 ppm ww; Figure 17.10). Although some NS&T sites were moved or not sampled in 1985 (Seal Beach was not sampled), similar concentrations and a similar pattern prevailed (Figure 17.11). In a separate 1984 survey employing methodologies comparable to those for NS&T Benthic Surveillance, Malins et al. (1986b) reported a total chlordane concentration of 0.2 ppm ww in liver of white croaker collected at the mouth of the Los Angeles River, with lower values elsewhere in the Los Angeles-Long Beach harbor area, Palos Verdes, and in Santa Monica Bay.

Together, these data indicate the recent existence of several inshore centers of chlordane contamination of fish liver, one in the Los Angeles-Long Beach harbor area (in the region between the Los Angeles River and Seal Beach) and one in central San Diego Harbor.

Only two other recent studies included measurement of dieldrin in fish. Dieldrin was measured in muscle tissue of seven taxa of marine organisms sampled from Upper Newport Bay in 1980 by SCCWRP (unpublished data). Concentrations were commonly at or below a detection limit of 0.001 ppm ww. However, some samples in all seven species groups exceeded detection limits for dieldrin, with the highest mean concentration in striped mullet (0.010 ppm ww; Table 17.4). On a dry weight basis, this mean concentration would be approximately 0.04 ppm dw, which is close to the level found in the most contaminated mussels measured in the NOAA NS&T 1986 sampling (0.03 ppm dw in *M. californianus* at Long Beach).
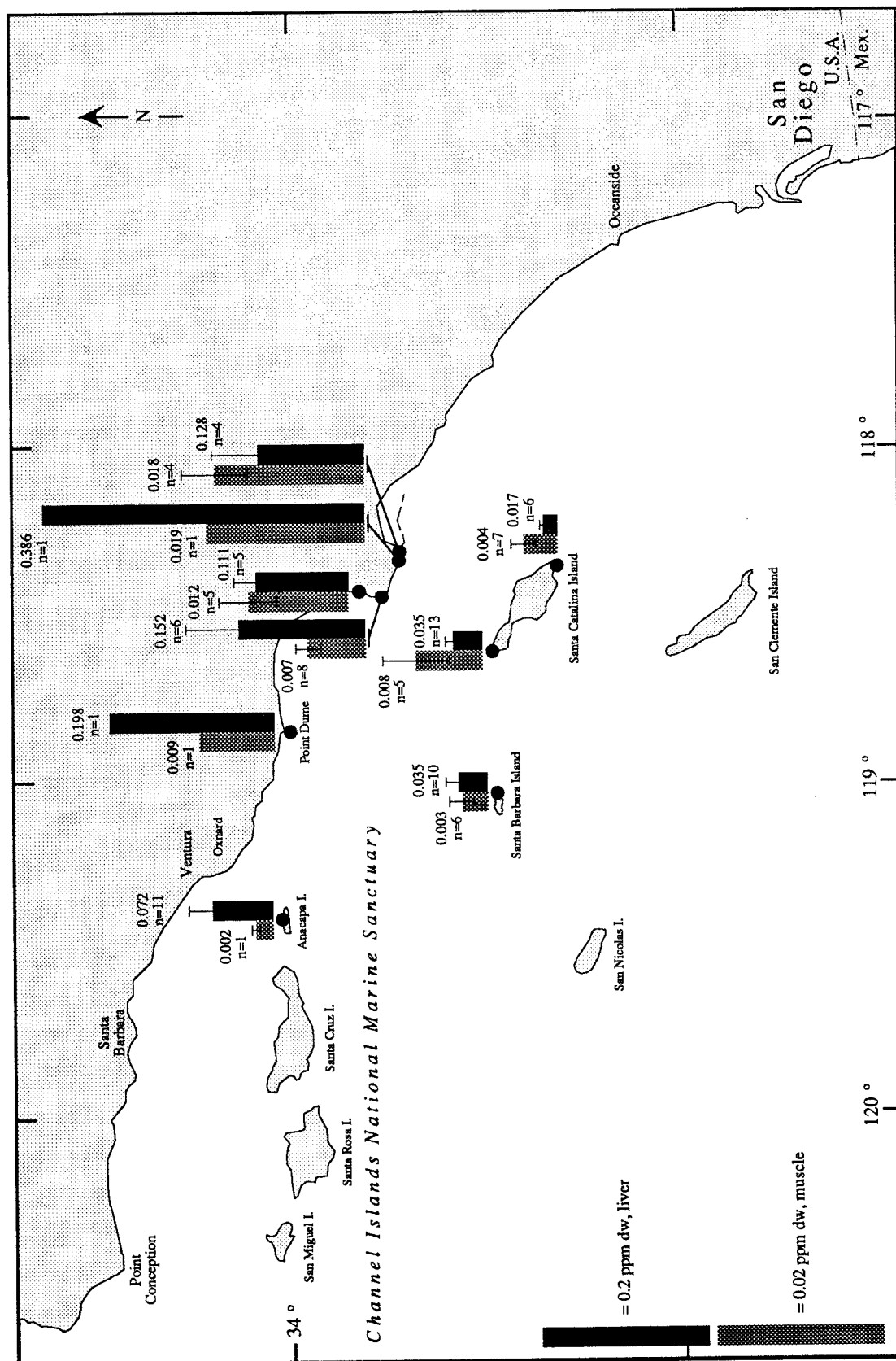
Figure 17.9. Dry weight concentrations of total chlordane measured in muscle and liver tissue of kelp bass sampled in the Southern California Bight in 1985. Note that scale for liver tissue is 10 times that for muscle. Source: Risebrough, 1987.
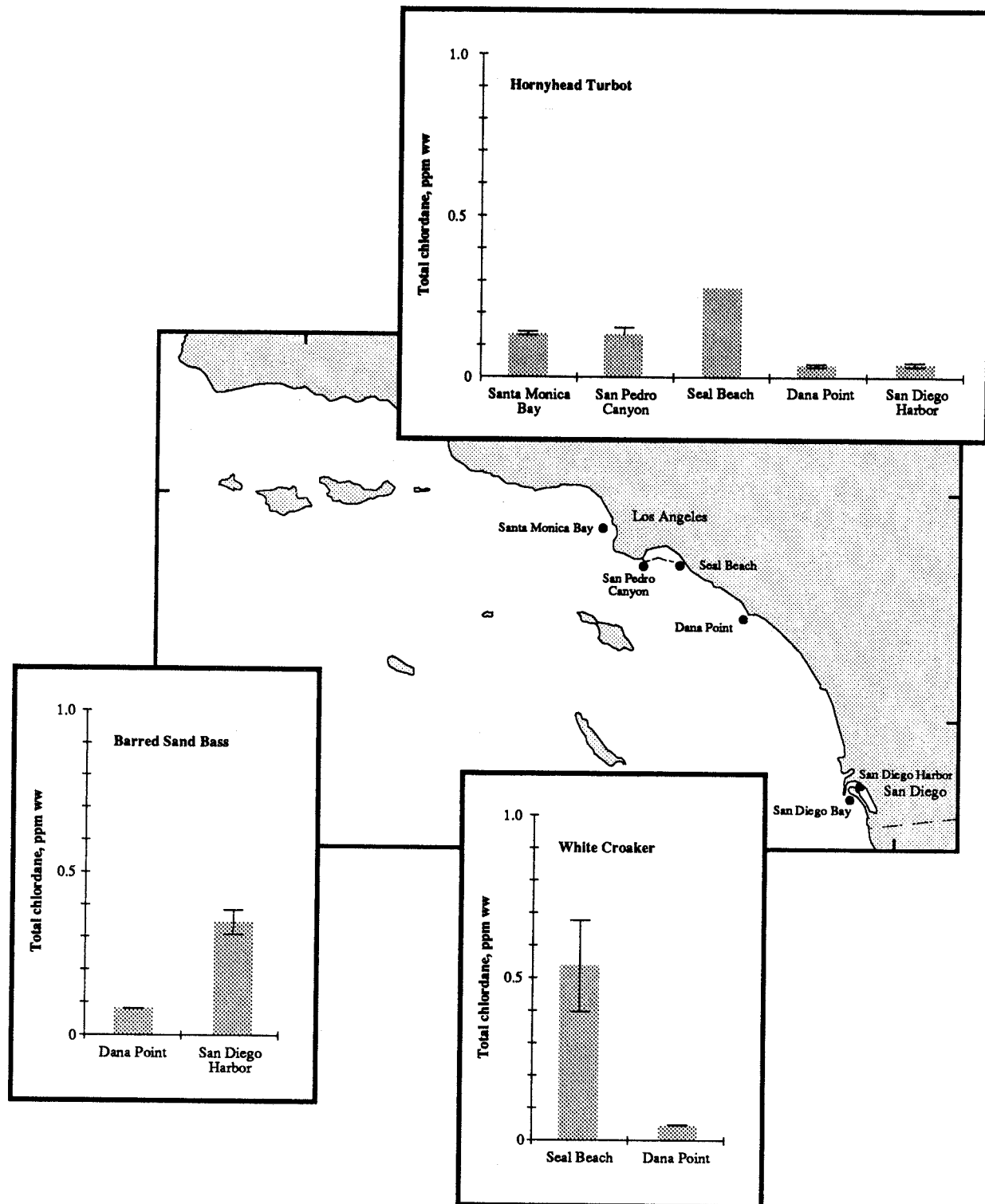
Figure 17.10. Concentrations of total chlordane measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.
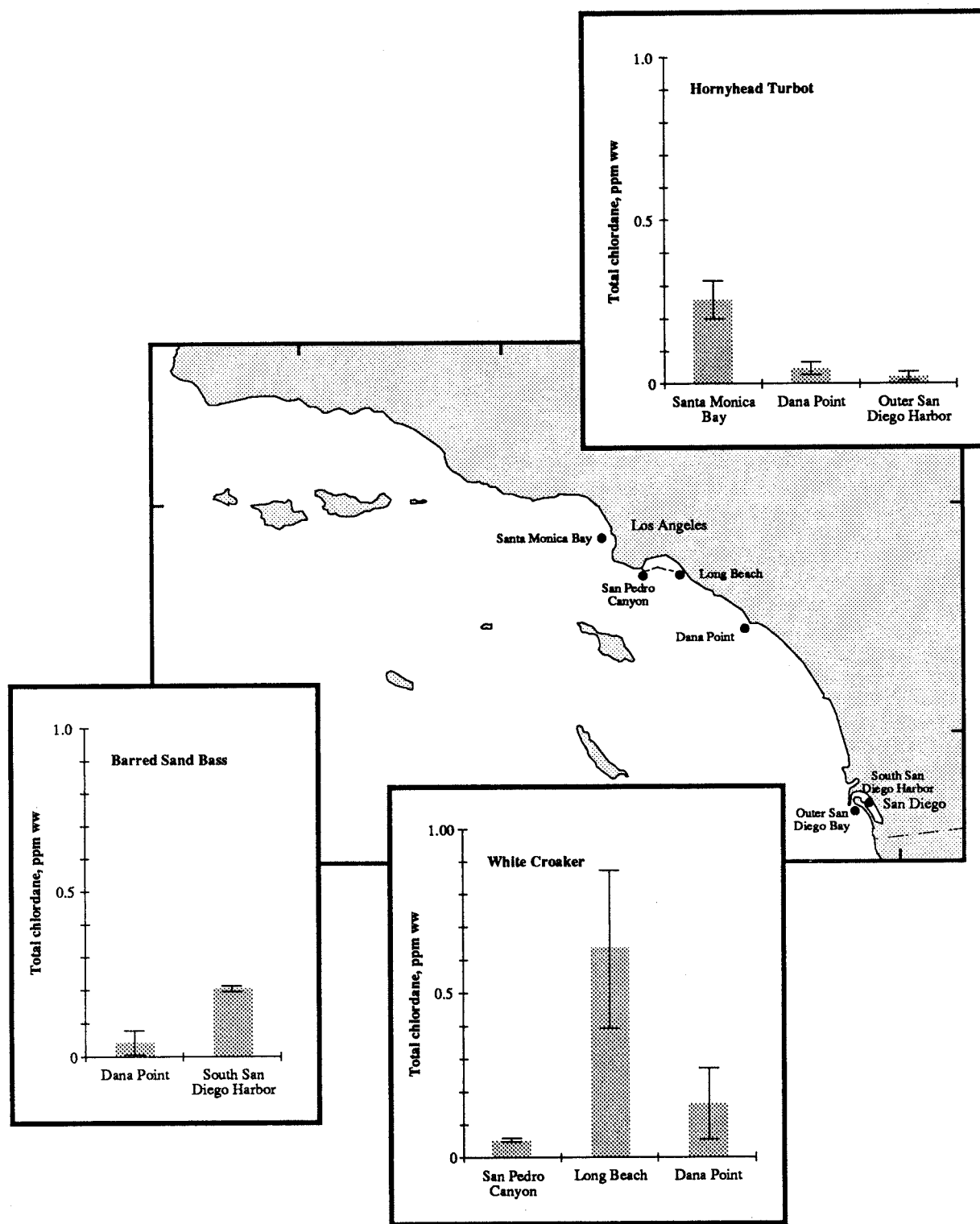
Figure 17.11. Concentrations of total chlordane measured in liver tissue of three fish species collected in the Southern California Bight in 1985. Source: Varanasi et al., 1988.

Table 17.4. Dieldrin concentration (ppm ww) in algae and in six species of marine organisms from Upper Newport Bay sampled in 1980. Unpublished data from SCCWRP based on samples collected by MBC and SCCWRP, 1980.

Common Name	No. of Samples	Mean	Median	Min	Max
Algae (2 species)	10	0.001	ND	<0.001	0.002
Shore crab	8	0.0015	0.002	0.001	0.002
Topsmelt	10	0.0014	0.001	<0.001	0.003
Longjaw goby (mudsucker)	8	<0.001	<0.001	<0.001	0.001
Striped mullet	10	0.0097	0.0085	<0.001	0.016
Yellowfin croaker	10	0.0019	0.001	<0.001	0.006
California halibut	10	<0.001	<0.001	<0.001	0.002

In the 1984 and 1985 NOAA NS&T Benthic Surveillance surveys, dieldrin concentrations in livers of southern California fish ranged from 0.002 in 1984 and 1985 in hornyhead turbot and white croaker from Dana Point to 0.072 in 1985 white croaker from Long Beach (Figures 17.12 and 17.13). These data suggest a possible gradient of increasing dieldrin concentrations approaching the Los Angeles-Long Beach harbors area (from Santa Monica Bay in the north and from Dana Point in the south), with a secondary area of elevated concentrations centered in San Diego Harbor in 1985 (barred sand bass, Figure 17.13).

The highest of the NS&T (1984-85) dieldrin concentrations were in the same range as several values reported in livers of rockfish from southern Santa Monica Bay and Cortez Bank (and in livers of spiny dogfish from southern Santa Monica Bay) from composites collected 14 years earlier by Duke and Wilson (1971). Species and concentrations in Santa Monica Bay were: starry rockfish, 0.09 ppm ww and spiny dogfish, 0.14 and 0.13 ppm ww. At Cortez Bank, liver values were: rosy rockfish, 0.06 and olive rockfish, 0.08 ppm ww. Finally, Duke and Wilson (1971) reported a dieldrin concentration of 0.23 ppm ww in fat tissue from the Santa Monica Bay starry rockfish. These data indicate that dieldrin has been a regionwide contaminant in the Bight.

While all the chlordane and dieldrin concentrations reported here seem to be low, they may, nevertheless, be significant. Relatively few samples exceeded the U.S. FDA action limit of 0.3 ppm ww for either pesticide. However, some international limits are more stringent, as low as 0.01 ppm ww for chlordane (Nauen, 1983). Thus, concentrations in some fish and shellfish from the Bight have occurred at levels of concern.
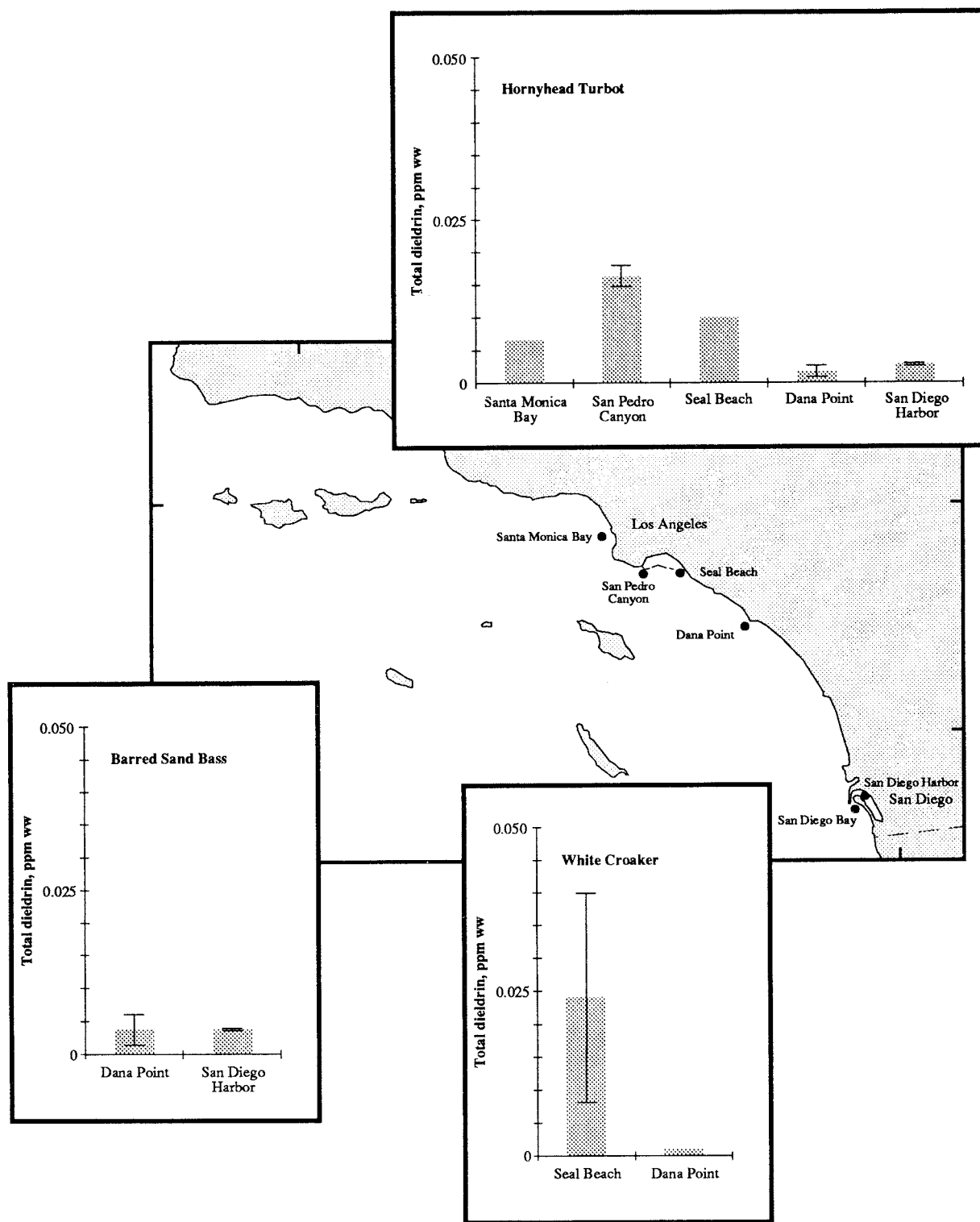
Figure 17.12. Concentrations of dieldrin measured in liver tissue of three fish species collected in the Southern California Bight in 1984. Source: Varanasi et al., 1988.
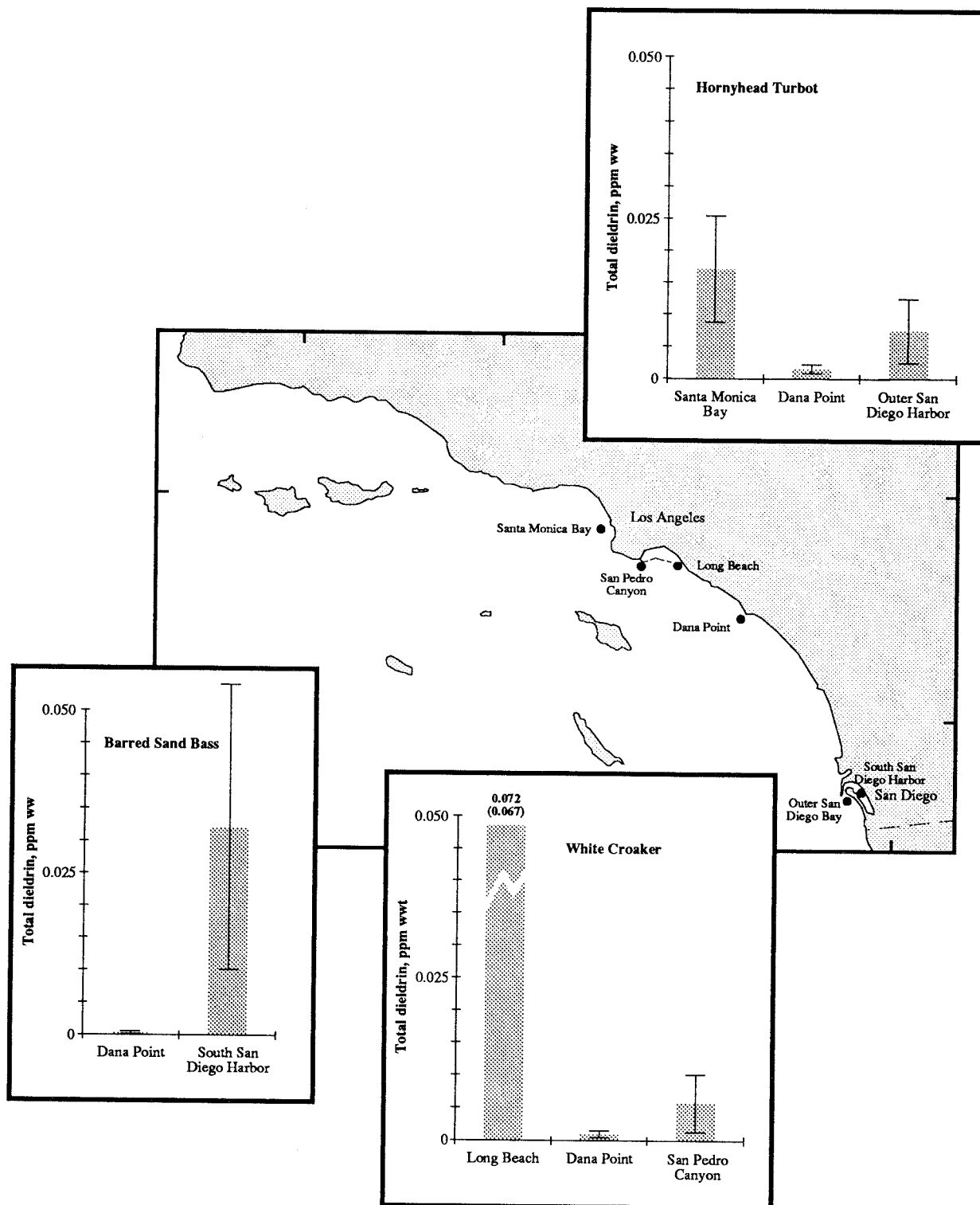
Figure 17.13. Mean concentrations of dieldrin measured in liver tissue of three fish species collected in the Southern California Bight in 1985. Source: Varanasi et al., 1988.

SUMMARY AND CONCLUSIONS

This discussion represents one of the few comprehensive overviews of chlordane and dieldrin contamination of sediments and marine life of the Southern California Bight. Together these data support previous CMW and University of Southern California Harbors Projects (Soule and Oguri, 1987) conclusions of chlordane contamination centers in Marina del Rey, the vicinity of Long Beach Harbor, and in southern San Diego Harbor. This analysis extends those observations to nearshore bottomfish (NS&T data) and reef fish (LARWQCB data). Data from sediments, mussels, and fish suggest that, unlike DDT, areas of elevated chlordane (and perhaps dieldrin) levels are inshore and not along the mainland shelf. The Palos Verdes region may have represented a possible exception in the past.

Tissue concentrations of chlordane or dieldrin about 0.001 to 0.01 ppm ww may be perceived to be of little environmental concern. However, given a federal action limit of 0.3 ppm ww, which was used to invoke a fishery closure in Maryland, such a range may be of significance. There is historical evidence that coastal fish (at Palos Verdes) exceeded this limit in the early 1970s. Given the higher concentrations in sediments and mussels in bays and harbors, and the propensity of chlordane to undergo biomagnification (Kawano et al., 1986), it is possible that fish in areas such as Colorado Lagoon, Marina del Rey, or San Diego Bay may contain muscle concentrations approaching or exceeding regulatory action levels.

CHAPTER 18

CONCLUSIONS AND RECOMMENDATIONS

This report described how much data exists for documenting the geographic distribution and long-term trends of 17 contaminants or groups of contaminants in sediments, mussels, fish, and other species of the Southern California Bight. By bringing together data from NOAA's NS&T Program and other survey efforts, it was possible to reconstruct some of the history of contamination for 10 trace elements, organotin compounds, PAHs, PCBs, and several pesticides.

This chapter concludes the report by summarizing geographic patterns and long-term trends of contamination, comparing and evaluating contaminants of concern, and providing recommendations for monitoring and supporting research.

STATUS: WHERE ARE THE HOT SPOTS AND THE CLEANEST AREAS?

The primary objective of this report was to place recent measures of contaminants, including those from the NS&T Program, into a regionwide perspective with emphasis on determining where sediments, mussels, and fish are contaminated and where they are not.

Defining the status of contamination is difficult; even though most of the areas reviewed in this report were surveyed more than once, most were not surveyed at the same sites during the same years. There is no "base" year from which to compare most of the sites of interest. Most were surveyed at least once between 1978 and 1986. Data collected after 1987 were not reviewed in depth for this report. Thus, it must be kept in mind that the conclusions about "status" in this report are focused primarily on the period 1980-86 and could easily be outdated by a new assessment.

Sediments

Sediments over most of the southern California mainland shelf have not been contaminated to concentrations of concern for any contaminants except DDT. Surprisingly, sediments of the Tijuana Estuary have relatively low concentrations of trace elements (in contrast to other bays). In addition to rural areas off the Santa Barbara-Ventura and Orange-San Diego county coastlines, relatively uncontaminated sediments have occurred at several outfall sites including off Oxnard, Orange County, and Point Loma. In fact, for PAHs and some trace metals, these are among the least contaminated urban coastal sediments in the United States.

However, there have been (through the mid 1980s) and remain several areas where contaminants, other than DDT, have been at concentrations of potential concern. These include all or portions of five bays and harbors: Marina del Rey; Los Angeles-Long Beach harbors; Bolsa Bay; Lower Newport Bay, especially near the shipyards in Rhine Channel; and the eastern shore of San Diego Harbor. Also included are two of the five major ocean outfall areas; the Palos Verdes shelf and central Santa Monica Bay (mainly along the 60-meter isobath). Offshore in deep water, it is probable that sediments around the wreck of the Pacific Baroness (sunk in 1987) remain at concentrations of concern for PAHs and copper.

It is instructive to evaluate further and compare the range of sediment contamination at several of the most well-surveyed locations. Median concentrations of nine contaminants in sediments from recent surveys at ten southern California sites are brought together in Table 18.1. A general scan of this table indicates several important features. This is not a complete list of sites and areas: bays and lagoons such as Mission Bay, Batequitos Lagoon, and marinas of Ventura County are missing. Data from these areas have either been overlooked in this review or it does not exist. There are no data for silver for many bays and harbors, or recent data for mercury in less-urbanized coastal areas such as the Santa Barbara or Port Hueneme shelf, or even at the Point Loma outfall site. Lack of data from possible reference areas puts a serious constraint on interpreting data from the urban and outfall areas.

Given these constraints, it appears that for most contaminants the most contaminated sites or regions have been in bays and harbors including Newport Bay shipyards (the Rhine Channel); San Diego Harbor, Santa Monica Bay, Marina del Rey, and Los Angeles-Long Beach harbors. The sediments of the coastal

shelf off Palos Verdes have also been highly contaminated. In these regions, concentrations of metals such as copper, lead, mercury, and zinc have been elevated by a factor of 3 or more above background or reference levels. In addition, several of these regions also have experienced the highest levels of contamination by PCBs, DDT, and PAHs. Sediments from Bolsa Bay have also contained high levels of DDT. The least contaminated coastal regions have been the Santa Barbara shelf and the shelf between southern Orange County and Point Loma.

A difficult question to address is the toxicity of sediments at the more contaminated sites. A detailed review of this question was not conducted. However, a range of possible answers is provided in Table 18.2. Sites where recent median sediment concentrations have exceeded the ER-M for many chemicals reviewed by Long and Morgan (1990) have included the Palos Verdes shelf (along the 60-meter isobath), Marina del Rey, Lower Newport Bay (especially near shipyards), Bolsa Bay, San Diego Harbor, and around the outfalls in Santa Monica Bay (60-meter isobath and deeper). Sediments around major outfall sites off Oxnard, Orange County, and Point Loma have not recently been contaminated above these ER-L concentrations.

Table 18.1   Median sediment concentrations at several southern California sites in recent years (ppm dw).

Site	Year	Cd	Cr	Cu	Pb	Hg	Ag	Zn	PCB	DDT
Newport shipyards	1986	-	31	550	140	11.3	-	295	-	-
Palos Verdes	1985	11	273	166	69	0.85	2	445	0.572	11
San Diego Harbor	1983	1.8	113	231	74	0.8	-	273	0.427	-
Marina del Rey	1985	0.5	47	82	143	0.67	-	192	-	0.047
Santa Monica Bay (60-m)	1985	3.5	55	26	88	-	-	35	0.106	0.044
Los Angeles-Long Beach harbors	1978	0.62	87	89	17	0.45	0.5	184	0.067	0.101
Upper Newport Bay	1980	0.8	29	26	23	0.06	0.5	113	0.01	0.18
Orange County Shelf outfall areas	1985	0.6	24	18	11	0.05	0.45	54	0.015	0.028
Point Loma outfall area	1985	1.1	20	18	19	-	0.9	46	0.0002	0.009
Santa Barbara Shelf	1985	0.2	31	7	4	-	0.01	47	0.014	0.018
Background Levels		0.4	29	10	10.5	0.05	-	44		

Table 18.2 Exceedances of ER-L and ER-M values (Long and Morgan, 1990) by median sediment concentrations measured in recent surveys (1978-87) in southern California. Confidence in ER-L and ER-M values for DDT, chlordane, and dieldrin should be considered low (Long and Morgan, 1990).

Contaminant	ER-L Value ppm dw	Exceedances	ER-M Value ppm dw	Exceedances
Arsenic	33	Palos Verdes (1985; 60-m) LA-LB harbors (1978)	85	None
Cadmium	5	Palos Verdes (1985; 60-m)	9	Palos Verdes (1985)
Chromium	80	Palos Verdes (1985; 60-m) LA-LB harbors (1973) Santa Monica Bay (1978) Marina Del Rey (1977)	145	Palos Verdes (1985)
Copper	70	Palos Verdes (1985) LA-LB harbors (1978) Newport Shipyards (1986) Marina del Rey (1987) San Diego Harbor (city side; 1987)	390	Newport Shipyards (1986)
Lead	35	Palos Verdes (1985; 60-m) Marina del Rey (1987) Santa Monica Bay (1985; 60-m) Bolsa Bay (1980)	110	Palos Verdes (1978) Marina del Rey (1987)
Mercury	0.15	Palos Verdes (1985) LA-LB harbors (1978) Lower Newport Bay (1971) Marina Del Rey (1987) Santa Monica Bay *1862(San Diego Harbor (1984) Point Loma (1975)	1.3	Palos Verdes (1973) Newport Shipyards (1986) Marina del Rey (1977)
Silver	1	Palos Verdes (1985; 60-m) Santa Monica Bay (1978; 60-m) San Diego Harbor (1983)	2.2	Palos Verdes (1978) Santa Monica Bay (1978)
Zinc	120	Palos Verdes (1985; 60-m) Newport Shipyards (1986) LA-LB harbors (1978) Marina del Rey (1987)	270	Palos Verdes (1988) Newport Shipyards (1986)
tPAH	4	<u>Pacific Baroness</u> (1988) Hyperion 7-mile (1986) South San Diego Harbor (1987)	30	<u>Pacific Baroness</u> (1988)
tPCB	0.05	Santa Monica Bay (1985); 60-m) Palos Verdes (1985) LA-LB harbors (1988) San Diego Harbor (1983)	0.4	Palos Verdes (1985) LA-LB harbors (1988) San Diego Harbor (1983)
tDDT*	0.003	All sites tested through 1987	0.35	Palos Verdes (1985) Bolsa Bay (1980)
Chlordane*	0.0005	Marina del Rey (1987) LA-LB harbors (1978) San Diego Harbor (1986) Palos Verdes (1985)	0.006	Marina del Rey (1987) San Diego Harbor (1986) Palos Verdes (1986)
Dieldrin*	0.00002	Marina del Rey (1986) LA-LB harbors (1978) Oceanside (1985)	0.008	LA-LB harbors (1978)

It should also be pointed out that the ER-L and ER-M values reported by Long and Morgan are guidelines describing the sediment toxicity and partitioning data evaluated in that report and are not toxicity criteria. Some are in considerable doubt. For example, while the ER-L for DDT (0.003 ppm dw) was very low and exceeded at all sites previously sampled in the Bight, Swartz et al. (1986) reported that a sensitive amphipod showed no observable effects when exposed to Palos Verdes sediments that contained 4.97 ppm DDE. Sensitive brittlestars were present in sediments containing 0.110 ppm, both several orders of magnitude above the ER-L. These observations suggest that this ER-L is inappropriate in southern California.

Mussels

Only some contaminants in mussels (DDT, PCBs, and chromium) appear to reflect the same contaminant patterns as revealed by sediments. High levels of these contaminants were found in mussels from Palos Verdes and San Pedro Bay. However, mussel surveys have identified additional areas of exceptional contamination by one or more chemicals. These include Oceanside Harbor (copper and zinc), Marina del Rey (copper, lead, mercury, silver, and zinc), San Diego Harbor (cadmium, copper, silver, tin, tPAH, PCBs, and DDT), and Lower Newport Bay (tin and DDT). Certain trace elements, notably cadmium and arsenic, are higher in mussels from remote areas than in those from presumably contaminated urban areas. Mussels naturally accumulate high levels of essential metals, including copper and zinc. It is therefore difficult to demonstrate that excess levels of these metals are due to anthropogenic inputs.

Fish and Shellfish

With the possible exception of tin in fish from San Diego Harbor, there is no indication of excess trace metal contamination in tissues of fish from any adequately sampled site. However, there are clear indications of depressed levels of metals in fish from several areas where sediments and mussels indicate contamination. On this point, the geographical patterns of contamination in fish livers from the 1984 NS&T Benthic Surveillance Program are in good agreement with historical patterns. Higher levels of arsenic, cadmium, chromium, copper, mercury, and selenium were found in fish from sites presumably remote from major metal inputs (such as Dana Point) as compared to sites near San Pedro Bay and San Diego Harbor. As suggested in the chapter on cadmium, there is some indication that high levels of organic contaminants (DDT) are correlated with depressed levels of some metals in mussels, and possibly in fish as well. A consequence of these patterns is the possibility that continued waste management activities in the Los Angeles area and San Diego Harbor may lead to decreasing levels of PCBs, DDT, and tin, but increasing levels of other trace elements in livers of nearshore bottomfish.

DDT, PCBs, tPAH, chlordane, dieldrin, and total tin are exceptions to the patterns observed for most metals. In data from NS&T and other programs, these contaminants are elevated in fish livers in approximate proportion to levels in nearby sediments or in mussels. Highest levels of these contaminants were detected in fish from Palos Verdes, San Diego Harbor, Los Angeles-Long Beach harbors, Santa Monica Bay, and Newport Bay.

LONG-TERM TRENDS: IS THE COAST CLEANER?

With one interesting exception, the long-term trend data reviewed for this report indicate that concentrations of contaminants are not increasing in sediments, mussels, or fish in the Bight. Taken in total, data reviewed for this report suggest that where they were once high, concentrations of most contaminants have been decreasing in sediments and tissues of marine organisms of the Bight. However, there are many major gaps in the trend monitoring data, most notably for bays, harbors, and lagoons where long-term monitoring has been virtually nonexistent. The one exception to the broad pattern of decreasing contamination with time is for cadmium in mussels from Royal Palms on the Palos Verdes Peninsula. Concentrations there have increased during the past 5 years despite reductions in emissions from a nearby sewage outfall. In spite of the many gaps in data and inconsistencies in sampling and analysis methods, the monitoring that has occurred has demonstrated the benefits of waste management activities that began in the 1970s.

Sediments

Where adequate time series or dated sediment core data exists, the data show that where concentrations of metals, DDT, PCBs and PAHs were once elevated, they have been declining. This includes sediments in offshore basins (Santa Barbara and San Pedro) and at some sites along the coastal shelf, including Santa Monica Bay, Palos Verdes, and at the Orange County outfall. Declines of levels of many contaminants (arsenic, cadmium, chromium, copper, mercury, zinc, PCBs, and DDT) in sediments from Palos Verdes have followed declines in emissions of these contaminants from a nearby sewage outfall. Decreases in lead and PAHs have also been noted in sediments from some areas. Unfortunately, there is inadequate information on temporal trends of selenium, silver, tin, chlordane, and dieldrin in sediment of the Southern California Bight.

Mussels

Again, where adequate time series exist, the data show that where concentrations of metals, DDT, and PCBs were once elevated, they have decreased since the 1970s. These trends are inferred largely from reconstructions at two coastal sites--Royal Palms (Whites Point) on the Palos Verdes Peninsula and at Oceanside. During the period 1977 to 1985, concentrations of DDT, PCBs, chromium, and lead clearly declined by factors of 2 to 10 at Royal Palms but were variable and at lower concentrations at Oceanside. In contrast, concentrations of silver, copper, mercury, and zinc were variable in Royal Palms and Oceanside mussels with no obvious long-term upward or downward trend. This lack of a trend does not follow the decreases in many of these metals seen in sewage effluent emissions and in sediment. Concentrations of these four trace elements were, and continue to be, higher in mussels from Royal Palms than from those at Oceanside. A rather startling additional observation, evident especially in the NS&T data, is for cadmium, which has been increasing at Royal Palms, but not at other sites, and which has been increasing as inputs from sewage have decreased. These observations suggest that, unlike chromium, lead, DDT, and PCBs, actual concentrations and interannual variations of cadmium, copper, mercury, and zinc in mussels at this site are independent of sewage inputs. Inadequate information exists to evaluate temporal trends in mussels for tin and selenium.

Fish and Shellfish

There is evidence that concentrations of DDT and PCBs have declined greatly in fish and shellfish of the coastal shelf. There is inadequate information to determine trends in concentrations of metals, PAHs, chlordane, and dieldrin in fish. However, since there is evidence that metals have not accumulated in fish and, in some cases, they have been depressed, there is little reason to expect concentrations to decline with time. Indeed, for some metals (cadmium) there may be reason to expect concentrations to increase in fish from areas such as Palos Verdes and San Diego Harbor. Many species of fish and other seafood invertebrates have been measured only once or twice during the past two decades. Without repeated surveys, it is impossible to judge the extent to which trends in inputs, sediments, and mussels are also reflected in the majority of important resource species.

CONTAMINANTS OF CONCERN: ONLY A FEW?

Which contaminants are of concern, which are not, and which have too many uncertainties for resolution? Five criteria were imposed on the data reviewed here:

1. Did the contaminant accumulate to excess or potentially toxic levels in sediments?

2. Did the contaminant accumulate in mussels at sites of known inputs or sediment accumulations?

3. Did the contaminant accumulate in fish or other species?

4. Is there evidence of biomagnification?

5. Is the contaminant increasing at sites within the Bight?

Specific attention was placed on contrasting existing and historical conditions at Palos Verdes with other areas.

As seen in Table 18.3, all contaminants or contaminant groups have accumulated in sediments at harbors and two outfall sites. However, not all contaminants have accumulated in mussels, macroinvertebrates, and fish. Only three contaminants (mercury, DDT, and PCB) showed clear evidence of biomagnification. Finally, existing evidence, where available, indicates that concentrations have been decreasing for 13 contaminants while the direction of trends remains uncertain for 2 of them.

Table 18.3. Summary of patterns of contamination in the Southern California Bight. "No" responses are intentionally left blank.

| Contaminant | Sediment? | Excess Accumulation in | | Fish? | Biomagni-fication | Increasing in Sediment or Biota |
		Mussels?	Macroinvertebrates?			
DDT	Yes	Yes	Yes	Yes	Yes	
PCBs	Yes	Yes	Yes	Yes	Yes	
PAHs	Yes	Yes	?	1		
Chlordane	Yes	Yes	?	Yes	?	
Tin	Yes	Yes	?	2	?	
Dieldrin	Yes	Yes	?	Yes	?	
Mercury	Yes	Yes			Yes	
Cadmium	Yes	Yes	Yes			3
Silver	Yes	Yes	Yes			?
Lead	Yes	Yes	?			
Selenium	Yes	?	?			
Chromium	Yes	Yes	Yes			
Copper	Yes	?	Yes			
Zinc	Yes					
Arsenic	Yes					

1- Parent compounds only
2- Organic Tin compounds only, trends in total tin are unknown
3- In mussels at Palos Verdes

Contaminants of Continuing Concern

Eight contaminants or classes of contaminants are of continuing concern and should be subject to continued or increased surveillance. These include four organic chemical classes: PAHs, PCBs, DDTs, chlordane and four trace elements: arsenic, lead, tin, and mercury. The organic chemicals and lead are clearly or largely anthropogenic in origin and have occurred in the Bight in marine organisms at concentrations of concern in terms of seafood quality or possible toxicity to marine organisms. In contrast, arsenic and mercury have also occurred at concentrations of concern in terms of seafood quality, but high concentrations are apparently *not* the result of known and/or controllable anthropogenic sources.

DDT, The extent of past DDT contamination of sediment and fish was incredible. In no other marine or coastal area of the United States have DDT concentrations in fish reached levels that have occurred historically in the Southern California Bight. DDT was an important regionwide contaminant of fish for at least a decade (1970-80). For example, concentrations of DDT in white croaker from Palos Verdes, which resulted in fishery advisories in 1985, once occurred 100 miles to the south near San Diego (Stout and Beezhold, 1980). These high levels were responsible for the near extermination of brown pelicans (Anderson *et al.*, 1977) and for the death of zoo seabirds fed locally caught fish (Young *et al.*, 1979). Had the 1985 level of concern been applied in 1970 and 1971, it is likely that the entire coast of southern California and beyond would have been posted with seafood consumption advisories. However, the most recent data suggest that the widespread occurrence of high levels in fish flesh is now restricted to the immediate coastline of the Palos Verdes Peninsula in large or older fish and in bottom fish in immediate contact with contaminated sediments.

DDT concentration apparently increases with trophic level. Highest levels have occurred in sharks and bottom fish. Concentrations in various fish appear to have decreased dramatically since the early 1970s. The principal reason for the sharp decrease is apparently control of emissions from the JWPCP outfalls at Whites Point (Royal Palms) off Palos Verdes. Although known inputs are now negligible, DDT remains in some species of fish from the Palos Verdes area, San Pedro Bay, and Santa Monica Bay. Concentrations may not appear to decrease as rapidly in large, long-lived fish, such as large kelp bass, as in younger kelp bass or in short-lived small species, such as perch. Therefore, it is not only important to continue monitoring DDT in sportfish from the Palos Verdes and appropriate reference areas, but to develop monitoring protocols that allow for prediction by age class or age group.

PCBs. PCBs have accumulated to potentially toxic levels in sediments from outfall areas such as Palos Verdes and bays and harbors such as Santa Monica Bay, San Pedro Bay, and San Diego Harbor. They are widespread contaminants of mussels and fish also, and recent assessments attribute most risk of cancer from consumption of contaminated seafood to PCBs. However, most evidence suggests that high levels of PCB contamination of fish have been more localized than DDT contamination in the Southern California Bight. Fish from Santa Monica Bay, Palos Verdes, San Pedro Bay, and San Diego Harbor have clearly been highly contaminated. In addition, PCB contamination increases with trophic level and highest levels of PCBs have been seen in sharks and bottom fish. Concentrations are lower now in fish from the Los Angeles area than in past years, but evidence is lacking to determine if concentrations have been decreasing or increasing in San Diego Harbor or have changed throughout the Bight as a whole. Also lacking is adequate data from other bay, harbor, and inshore areas (especially Port Hueneme, Marina del Rey, inner San Pedro Bay, Huntington Harbor, Newport Bay, and the lagoons of San Diego County).

A possible impediment to tracking declining PCB levels in coastal fish and macroinvertebrates is the high detection limit (0.2 ppm ww) for PCBs imposed in monitoring programs of some dischargers. For example, muscle of most fish sampled in the Orange County monitoring program contain PCBs at concentrations below this detection limit. In the past, detection limits were lower (0.001 to 0.01 ppm ww). If detection limits are not soon reduced to their earlier values, there will be no useful record of reduction due to continuing source control.

PAHs. Since they are potent carcinogens, PAHs are of concern wherever they are found. In the data reviewed here for the Southern California Bight, one or more higher molecular weight PAHs (such as B(a)P) have been measured in sediments, mussels, and/or fish from several areas: Santa Monica Bay near the now abandoned sludge outfall; San Pedro Bay and the adjacent Palos Verdes shelf and San Pedro Basin; in San Diego Harbor; and in several smaller harbors. Beyond these sites, along the open coast and in the few island sites that have been surveyed, PAHs do not accumulate in sediments or mussels. Although PAHs do not accumulate in fish, measures of PAH metabolite compounds in bile of benthic fish from several harbor areas of the Southern California Bight have shown that fish are exposed to PAHs. Temporal trends in PAH levels remain uncertain, but may have declined.

Appropriate measures of PAHs or their metabolites should be continued to determine if concentrations are increasing or decreasing. Additional harbors and urbanized embayments should be sampled, especially Newport Bay. It is critical to continue to monitor the same recently sampled sites, species, and substrates.

Chlordane. Concentrations of chlordane in sediment from Marina del Rey, Palos Verdes, and San Diego Harbor have exceeded those that are potentially toxic to sensitive marine species. Clearly chlordane compounds have entered marine ecosystems of the Bight. Chlordane may biomagnify. Although concentrations in edible tissues have not exceeded FDA guidelines, some were close. Exceedances may have occurred in previous years (early 1970s) in fish near the Los Angeles area. Many areas have not been surveyed for chlordane in fish or other seafood organisms, but data from mussels in Marina del Rey suggest that fish from all urban harbors should be measured. Long-term trends in chlordane concentrations remain unknown. Since chlordane is apparently toxic to sensitive species at very low concentrations, detection limits for sediments should be correspondingly low.

Mercury. Mercury has accumulated in sediment from several areas (especially at Palos Verdes, Newport Bay, and Marina del Rey) at concentrations that may have been toxic to some benthic invertebrate species. Mussels from Marina del Rey have contained elevated levels of mercury. Mercury occurs naturally in high concentrations in fish from many areas and there is strong evidence that some species contain mercury far more than the FDA action limit of 0.5 ppm ww. Mercury increases with trophic level. For example, all sharks and some fish yielded one or more samples of flesh at or far above (up to 20 times) the FDA limit. Although mercury in sediment has declined in response to source controls, temporal trends in mussels and fish remain uncertain. Since the highest levels of mercury were seen in fish from areas located far from known sources, it does not appear that mercury from coastal waste discharges is responsible for concentrations observed in fish. Thus, the only management action possible is to conduct adequate surveys of large fish and sharks and warn consumers as appropriate. It would be useful to conduct mercury surveys to identify species and sizes of fish, sharks, and rays that meet federal or local guidelines.

Arsenic. Although accumulations of arsenic in sediment have not reached potentially toxic levels, arsenic occurs naturally in high concentrations in selected species of mollusks, fish, and crustaceans. Arsenic concentrations in certain fish are sufficiently high to cause concern from a consumer standpoint. Arsenic concentrations in flatfish, particularly Pacific sanddab, are high, especially in areas remote from urban pollution sources. Concentrations are depressed in some species from polluted areas. Arsenic concentrations in sediment have declined, but no change has been noted in mussels or fish. The source of high levels of arsenic in certain species in unknown, but it does not appear to be from anthropogenic sources and may, like mercury, be a natural phenomenon. It is thought that arsenic in fish and shellfish exists in the less-toxic organic form, but the risk to human health from consuming these concentrations of arsenic is unknown. Accordingly, the only effective management action is to survey arsenic adequately in fish from the Bight and post advisories as appropriate.

Lead. Lead has clearly contaminated sediments and mussels of the Los Angeles, Orange County, and San Diego County coastal areas for many years. Concentrations of lead in sediments of Palos Verdes, Newport Bay, San Diego Harbor, and Marina del Rey may have been high enough to cause toxicity in sensitive species. In the 1970s, concentration gradients in mussels reflected the importance of aerial fallout from auto emissions as a major source. Concentrations in mussels declined during the late 1970s but have leveled off and remained unchanged during the 1980s despite continued reductions in sewage effluents and resultant decreases in sediment concentrations. Concentrations are still as much as 5 times higher in mussels from Palos Verdes than in those from Oceanside, suggesting continued inputs from the Los Angeles area, presumably from aerial fallout. New measurements of lead (using ultraclean facilities) in tissues of fish and macroinvertebrates are needed to determine if concentrations have changed since the late 1970s. Most existing recent tissue data (except from mussels) is invalid for this comparison unless it can be demonstrated that samples were prepared and analyzed in a lead-free environment.

Contaminants of Uncertain Concern

There are five contaminants of uncertain concern, each for a different reason.

Phenol. Phenol was not a target chemical for this review, but may be important since quantifiable concentrations appeared in fish from the Los Angeles and Orange County areas during surveys conducted in the early 1980s. A review of phenol inputs and distribution may reveal a need for additional measurements.

Organotin Compounds and Tin. Organotin compounds are clearly contaminants in sediments of San Diego Harbor, San Pedro Bay, Marina del Rey, Oxnard Harbor, and Palos Verdes. Levels of tin in mussels have been highest in Newport Bay and San Diego Harbor. Highest levels of tin have been seen in fish from San Diego Harbor although trends with time have not been well investigated. Surveys should expand into other marinas and a concerted effort should be made to measure organotin concentrations in livers of fish from these areas. At the same time, data should be obtained on total or inorganic tin concentrations to quantify any consistent relationship to organotins.

Cadmium. Cadmium has accumulated in sediments and may have occurred at toxic levels at Palos Verdes. Elevated concentrations of cadmium have been measured in San Diego Harbor. Cadmium does not appear to accumulate in fish or undergo biomagnification. Mussels and fish from islands and remote sites in the Santa Barbara area generally contained higher levels than those from the more urban areas. However, macroinvertebrates from Palos Verdes have contained higher levels of cadmium than those from more remote areas. There is some evidence to conclude that cadmium is increasing in mussels at Palos Verdes. There may be an inverse relationship between concentrations of cadmium in mussels and DDT contamination.

Silver. Silver has accumulated in sediment from many areas and may have existed at toxic levels at Palos Verdes and Santa Monica Bay. Results of silver analyses show a meso-scale gradient in mussels along the coast from central California to northern Baja California. The presumption is that silver inputs from sewage have, like DDT, spread over large areas of the coast. The dilemma is that unlike DDT there is evidence that silver is not accumulating in edible tissues of most seafood organisms. However, organisms from truly remote areas of Baja California or central California have not been measured so it may be premature to conclude a gradient similar to that in mussels does not also exist in fish. Levels of silver in sediment and mussels have apparently not changed with time. Trends in fish are unknown.

Contaminants Apparently Not of Concern

Existing evidence indicates that four metals and large numbers of organic chemicals undergo neither bioaccumulation nor biomagnification in fish of the Bight, or that elevations in macroinvertebrates are, or have been, extremely localized and not of regional significance.

Chromium, Copper, and Zinc. These trace metals do not accumulate or biomagnify in fish or most macroinvertebrates in the Bight. Tissues of several species of shellfish at Palos Verdes were once contaminated with these metals. It might be worthwhile to resample them once to confirm that concentrations have decreased commensurate with known reductions in emissions. This was a local, not a regional phenomenon.

Dieldrin. Dieldrin may have once been a contaminant of concern in the Bight, but existing data, although sparse, does not indicate important concentrations of dieldrin in any substrate.

Volatile and Extractable Organics. Although not reviewed in depth, data on several dozen volatile organic compounds measured during the past 5 years as part of the CSDOC monitoring program, indicate that none of these compounds have accumulated in fish or shellfish (chapter 3). The lack of bioaccumulation of most volatile and extractable organic chemicals in fish and macroinvertebrates of the Bight is not surprising due to their low partitioning coefficients and volatility. However, many may still be important as toxicants in water and at the sea surface in local areas of heavy inputs.

RECOMMENDATIONS FOR MONITORING AND ASSESSMENT

Continue Monitoring

More than 18 million dollars have already been spent annually on ocean monitoring in the Southern California Bight during the past two decades. While there are many incompatibilities among the contaminant surveys, they nonetheless, represent a remarkable monitoring achievement and a record of contamination and recovery that is continuing today. These data should be made available to all agencies through some type of regional archive. In this way, opportunities for extending time series will be made more readily apparent and will provide points of reference for marking the further progress of reductions in contaminant loading.

Compared to the history of contaminant monitoring in the Bight, NOAA's NS&T Program is relatively young and much of the data is not yet available for long-term assessment. However, existing data can provide some insight into what to expect in the future and can also confirm whether NS&T sites are appropriately placed and the extent to which patterns in NS&T data reflect regional patterns. Existing monitoring programs, especially those conducted by dischargers, should be better coordinated to ensure that results are comparable to those from other current and historical monitoring programs.

Improve Species Assessments

Hundreds of species from the Bight have been subjected to chemical analyses. However, with the exception of mussels, routine measurements have been made on relatively few species. For example, the longest contemporary time series for fish has been the annual-to-triennial monitoring of kelp bass, black perch, and Dover sole at Palos Verdes as conducted by the CSDLAC. Data for kelp bass and Dover sole were reviewed in this report (for DDT and PCBs). Beyond this, there has been no continuous species-specific sampling for shelf fish or macroinvertebrates and no continuous sampling in harbors. With the notable exception of mussels, there is no long-term trend available for any species at a control or reference site remote from sewage outfalls.

More time series of contamination could be developed if monitoring and research agencies resampled historically important species and reoccupied historical sites. The three-decade time series of DDT in mesopelagic fish by MacGregor (1974) could be extended by nearly two decades if mesopelagic fish were resampled. The trend in contamination of intertidal and subtidal macroinvertebrates at Palos Verdes could be extended through a resurvey similar to that reported in the state seafood survey (Young et al., 1978). Important trends for PCB and DDT could be updated by resampling Dover sole at several points along the coast in addition to Palos Verdes.

Mollusks other than mussels, and some crustaceans may be better indicators of metal contamination than either mussels or fish. It may be useful to conduct a regionwide survey of contaminants in species such as scallops, prawns, crabs, and lobsters including representative or related species in harbors and bays.

Future analyses of contaminants in biota should include assessments of lipid content to allow the exploration of relationships between lipid-normalized tissue concentrations and sediment concentrations.

Improve Site Selection

With the exception of compulsory monitoring at sewage outfall sites and monitoring at several CMW sites, there has been no continuing regionwide monitoring of contaminants in the Southern California Bight. Instead, there has been a long history of aperiodic independent surveys of contaminants in sediments, mussels, or fish. With the exception of a few surveys, there has been no regionwide attempt to measure contaminants simultaneously in two or more substrates so that relationships between them can be determined or convincingly rejected. Further, few surveys have sampled sediments, mussels, or fish simultaneously in harbors, along the coastal shelf, and at offshore island sites. Instead, harbors and bays, or small portions of them, have been surveyed independently and with varying degrees of effort. As a result, it is difficult to make direct comparisons among harbor, shelf, and island sites.

It is also difficult to identify what control, reference, or baseline concentrations should be in sediments, mussels, macroinvertebrates, and fish in bays, on the shelf, and at offshore islands. It is possible each of these ecosystems has different background levels for naturally occurring metals and PAHs in sediments and various organisms. Missing from the regional data base is a suite of contaminant data from a clearly remote region that could include sediment, invertebrate, and fish samples from a bay, the shelf, or offshore island, and the pelagic environment. A reference transect in northern or central Baja California might provide the desired information. Historically, however, harbors and bays have not received the intensive surveillance and monitoring as has been undertaken along the coastal shelf. Contaminant data from bays and harbors remain fragmentary and frequently incomparable in terms of analytes sought. Many marinas and lagoons have yet to be adequately sampled. Accordingly, a synoptic survey of contaminants in harbor sediments and marine life appears to be needed.

Improve Chemical Techniques

Methods of analysis should be improved for some contaminants. For example, analyses of lead in tissue samples should be conducted in a lead-free laboratory environment and marine organisms collected using lead-free techniques. Detection limits for PCBs, DDT, chlordane, and dieldrin must be sufficiently low to allow comparisons with historical data and to evaluate the potential for toxicity to sensitive species. Detection limits for many contaminants in waste water are now too high to estimate emission rates. Since levels of contaminants in waste water apparently are continuing to decline, other sources of contaminants should be quantified. Improved methods of estimating the magnitude of aerial fallout and runoff of contaminants are needed. When new analysis methods are developed, split samples should be analyzed using old and new methods to evaluate the comparability of results between the two methods.

The relationship between concentrations of cadmium and organic contaminants in mussels, fish, and other species should be further investigated to determine whether cadmium levels in fish or mussels might be expected to increase in response to declines in DDT or PCB concentrations.

Improve Bioaccumulation Information

There have been several attempts to develop predictive tools to assess the availability of sediment contaminants to infauna or bottom fish. These tools could be used to develop sediment quality criteria and estimate the magnitude and extent of expected contamination in species that associate with sediments. For example, the relationship between AVS-normalized sediment metal concentrations and concentrations in bottom fish should be further investigated. Also, the relationship between lipid-normalized organic contaminants in fish and TOC-normalized concentrations in sediment should be explored further.

Data Inventory and Management

It is a cumbersome job to identify, acquire, extract, evaluate, and analyze all the existing and ongoing monitoring data from a major urban region such as the Southern California Bight. However, to track progress in pollution control, it is necessary that this work be done on an ongoing basis by a central regional authority. A true centralized regional data base and data base management system are costly and expensive activities. At a minimum however, some centralized regional authority should at least inventory monitoring activities and annually publish an account of the status and fate of agency monitoring activities, data products, and performing laboratories. To underscore the need for this, we wish to note that several existing data sets reviewed for this report were nearly discarded by the performing agency following the death of the principal investigator. Other major local and national data sets were difficult to interpret without direct discussions with the principal investigators, several of whom had already retired from public service. Many more scientists and technicians who performed monitoring and research surveys during the 1970s and 1980s will soon be retiring or making career changes and there is little guarantee that the existing data will be properly maintained or made accessible. To avert future tragic loss of this valuable information, it is vital that regional, state, and federal authorities make explicit commitment for ensuring the integrity and accessibility of existing data. Once a data set is lost, there will be no opportunity to evaluate whether it could have helped in future trend assessments.

CONCLUSION

The most important conclusion from the collective data is that with the exception of the Palos Verdes Peninsula, harbors and bays have been the most contaminated sites in the Bight. This is not surprising considering their proximity to urban, industrial, and residential areas and their restricted circulation. Highest levels of DDT, PCBs, copper, lead, mercury, and zinc have been found in sediments from Newport Bay, San Diego Harbor, Santa Monica Bay, Marina del Rey, Los Angeles-Long Beach harbors and, of course, Palos Verdes. Biological effects surveys can most fruitfully be focused on these areas. The least contaminated areas for sediments are the coastal shelf areas near Santa Barbara and between southern Orange County and Point. Loma. Only some contaminants (chromium, DDT, and PCBs) show the same pattern in mussels as in nearby sediments. Highest levels of these contaminants were found at Palos Verdes and San Pedro Bay. Mussels from Oceanside Harbor, Marina del Rey, San Diego Harbor, and Newport Bay also contained elevated levels of contaminants, but in different patterns than those in sediment. In fish, only the organic contaminants show a similar pattern to that in sediments or mussels. Highest levels were found in

the above mentioned bays and harbors. For most metals, highest levels were found in fish from areas remote from known sources, such as Dana Point.

For many of the chemicals reviewed here, concentrations in sediments have declined dramatically since the early 1970s, especially at the Palos Verdes Peninsula. Where they were once elevated, concentrations of many contaminants in mussels and fish have also declined, although there is less information available to support this conclusion. The only contaminant that has apparently increased in concentration in recent years is cadmium in mussels from Palos Verdes.

Five criteria were imposed to determine which contaminants are of continuing concern in the Southern California Bight:

1. Accumulations to excess or potentially toxic levels in sediment.

2. Accumulation in mussels.

3. Accumulation in fish or other species.

3. Biomagnification.

5. Long-term trend of increasing concentrations in sediment, mussels, or other species.

There was evidence that all contaminants have accumulated in sediment, particularly in bays and harbors. However, not all have accumulated to potentially toxic levels. Also, not all contaminants have accumulated in mussels and other species. Only three contaminants showed evidence of biomagnification. Finally, only one compound is apparently increasing in concentration. The chemicals of concern in the Southern California Bight that can be managed by further controlling inputs are DDT, PCBs, chlordane, lead, and PAHs. Mercury and arsenic are naturally high in some species and, while of possible public health concern, cannot be managed through control of regional sources. Those of uncertain concern include tin, cadmium, and silver. Contaminants that are apparently not of concern include chromium, copper, zinc, and dieldrin.

APPENDIX A

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APPENDIX B

COMMON AND SCIENTIFIC NAMES OF MARINE ORGANISMS
FROM THE SOUTHERN CALIFORNIA BIGHT

COMMON NAME	SCIENTIFIC NAME

Algae

algae, brown	*Egregia*
algae, green	*Chlorephycae*
algae, red	*Sargassum*
kelp	*Macrocystis pyrifera*
kelp, giant	*Macrocystis pyrifera*
phytoplankton	*Neanthes arenaceodentata*
Sea lettuce	*Ulva*
zooplankton	*Acartia californiensis*

Invertebrates

abalone, red	*Haliotis rufescens*
abalone, black	*Haliotis crachcrodii*
amphipods	*Ampelisca abdita*
	Rhepoxynius abronius
brittlestar	*Amphiodia urtica*
bryozoan	*Bugula*
clam, fat gaper, horse	*Tresus nutalli*
clam , tellin	*Tellina*
crab, pointer	*Mursia guadichaudii*
crab, purple shore	*Hemigrapsus nudus*
crab, sand	*Emerita analoga*
crab, striped shore	*Pachygrapsus crassipes*
crab, yellow	*Cancer anthonyi*
euphausiid	*Nematoscelis sp.*
hydroid, ostrich plume	*Agloaphenia*
lobster, California spiny	*Panulirus interruptus*
mussel, bay	*Mytilus edulis*
	Mytilus galloprovincialis
mussel, California	*Mytilus californianus*
mussel, ribbed horse	*Modiolus demissus*
octopus	*Octopus*
oyster	*Ostrea sandvicensis*
oyster, eastern	*Crassostrea virginica*
oyster, European	*Ostrea edulis*
oyster, Pacific	*Crassostrea gigas*
polychaetes	*Polychaeta*
prawn, ridgeback	*Sicyonia ingentis*
scallop, rock	*Hinnites multirugosus*
scallop, purple hinge	*Hinnites multirugosus*
sea cucumber	*Parastichopus californicus*
sea slug	*Navanax ineris*
sea skater	*Halobates sp.*
sea star	*Luidia foliolata*
sea urchin, green	*Strongylocentrotus droebachiensis*
sea urchin, purple	*Strongylocentrotus purpuratus*
sea urchin, red	*Strongylocentrotus franciscanus*
shrimp	
shrimp, caridean	*Eucerida decapoda*
shrimp, mysid	*Mysidae sp.*
shrimp, sergestid	*Sergestes sp.*

COMMON NAME	SCIENTIFIC NAME

Invertebrates

snail	*Haliotis*
snail, kelp	*Norrisia norrisii*
squid, common market	*Loligo opalescens*
star	*Pisaster brevispinus*
anchovy, northern	*Engraulis mordax*

Bony Fish

barracuda, Pacific	*Sphyraena argentea*
bass, barred sand	*Paralabrax nebulifer*
bass, kelp	*Paralabrax clathratus*
bass, sand	*Paralabrax sp.*
bass, spotted sand	*Paralabrax maculatofasciatus*
bass, striped	*Morone saxatilis*
blacksmith	*Chromis punctipinnis*
bocaccio	*Sebastes paucispinis*
bonito, Pacific	*Sarda chiliensis*
cabezon	*Scorpaenichthys marmoratus*
combfish, longspine	*Zaniolepis latipinnis*
corbina, California	*Menticirrhus undulatus*
croaker, black	*Cheilotrema saturnum*
croaker, white	*Genyonemus lineatus*
croaker, yellowfin	*Umbrina roncador*
eelpout, midwater	*Melanostigma pammelas*
flatfish, unidentified	*Pleuronectidae sp.*
flounder, winter	*Pseudopleuronectes americanus*
Garibaldi	*Hypsypops rubicundus*
Goby, (mudsucker), longjaw	*Gillichthys mirabilis*
grunion, California	*Leuresthes tenuis*
hake, Pacific	*Merluccius productus*
halfmoon	*Medialuna californiensis*
halibut, California	*Paralichthys californicus*
halibut, Pacific	*Hippoglossus stenolepis*
hatchetfish	*Argyropelecus sp.*
lampfish, northern	*Stenobrachius leucopsarus*
lightfish, bristlemouth	*Cyclothone sp.*
lingcod	*Ophiodon elongatus*
lizardfish, California	*Synodus lucioceps*
mackerel, chub (Pacific)	*Scomber japonicus*
mackerel, jack	*Trachurus symmetricus*
midshipman, plainfin	*Porichthys notatus*
midshipman, specklefin	*Porichthys myriaster*
mullet , striped	*Mugil cephalus*
opaleye	*Girella nigricans*
perch, black	*Embiotoca jacksoni*
perch, white	*Phanerodon furcatus*
perch, pile	*Rhacochilus vacca*
queenfish	*Seriphus politus*
ratfish, spotted	*Hydrolagus colliei*
rockfish , rosy	*Sebastes rosaceus*
rockfish	*Sebastes sp.*
rockfish, aurora	*Sebastes aurora*
rockfish, blackgill	*Sebastes melanostomus*
rockfish, blue	*Sebastes mystinus*
rockfish, brown	*Sebastes auriculatus*

COMMON NAME	SCIENTIFIC NAME
Bony Fish	
rockfish, calico	*Sebastes dalli*
rockfish, copper	*Sebastes caurinus*
rockfish, flag	*Sebastes rubrivinctus*
rockfish, gopher	*Sebastes carnatus*
rockfish, gray	*Sebastes brevispinis*
rockfish, greenspotted	*Sebastes chlorostichtus*
rockfish, greenstriped	*Sebastes elongatus*
rockfish, olive	*Sebastes serranoides*
rockfish, splitnose	*Sebastes diploproa*
rockfish, starry	*Sebastes constellatus*
rockfish, stripetail	*Sebastes saxicola*
rockfish, vermillion	*Sebastes miniatus*
rockfish, whitebelly	*Sebastes vexilaris*
sablefish	*Anoplopoma fimbria*
salmon, king	*Oncorhynchus tshawytscha*
sanddab, gulf	*Citharichthys fragilis*
sanddab, longfin	*Citharichthys xanthostigma*
sanddab, Pacific	*Citharichthys sordidus*
sanddab, speckled	*Citharichthys stigmaeus*
sardine, Pacific	*Sardinops caeruleus*
saury, Pacific	*Cololabis saira*
scorpionfish, California (sculpin)	*Scorpaena guttata*
sculpin, yellowchin	*Icelinus quadriseriatus*
seabass, white	*Atractoscion nobilis*
seaperch, pink	*Zalembius rosaceus*
seaperch, rainbow	*Hypsurus caryi*
seaperch, rubberlip	*Rhacochilus toxotes*
seaperch, white	*Phanerodon furcatus*
sheephead, California	*Semicossyphus pulcher*
smelt, jack	*Atherinopsis californiensis*
smelt, top	*Atherinops affinis*
smoothtongue, California	*Leuroglossus stilbius*
sole, bigmouth	*Hippoglossina stomata*
sole, C-O	*Pleuronichthyes coenosus*
sole, Dover	*Microstomus pacificus*
sole, English	*Parophrys vetulus*
sole, fantail	*Xystreurys liolepis*
sole, rex	*Glyptocephalus zachirus*
sole, slender	*Lyopsetta exilis*
surfperch, barred	*Amphistichus argenteus*
surfperch , walleye	*Hyperprosopon argenteum*
surfperch, shiner	*Cymatogaster aggregata*
swordfish	*Xiphias gladius*
thornyhead, longspine	*Sebastolobus altivelis*
thornyhead, shortspine	*Sebastolobus alascanus*
tonguefish, California	*Symphurus atricauda*
treefish	*Sebastes serriceps*
tuna, albacore	*Thunnus alalunga*
tuna, yellowfin	*Thunnus albacares*
turbot, diamond	*Hypsopsetta guttulata*
turbot, hornyhead	*Pleuronichthys verticalis*
whelk, kellets	*Kelletia kelletii*
whitefish, ocean	*Caulolatilus princeps*
wrasse, rock	*Halochoeres semicinctus*
Yellow tail	*Seriola lalandei*

COMMON NAME	SCIENTIFIC NAME

Sharks and Rays

dogfish, spiny	*Squalus acanthias*
ray, bat	*Myliobatis californica*
shark, basking	*Cetorhinus maximus*
shark, blue	*Prionace glauca*
shark, thresher	*Alopias vulpinus*
shark, mako	*Isurus oxyrinchus*
shark, white	*Carcharodon carcharias*

Mammals

sea lion, California	*Zalophus californianus*
sea lion, northern	*Eumetopias jubata*
seal, Guadalupe fur	*Arctocephalus townsendi*
seal, harbor	*Phoca vitulina*
seal, northern elephant	*Mirounga angustirostris*
seal, northern fur	*Callorhinus ursinus*

APPENDIX C
ACRONYMS AND ABBREVIATIONS

AAS	atomic absorption spectrometry
Ag	silver
Al	aluminum
Am	americium
As	arsenic
AVS	acid volatile sulfide
B	boron
B(a)p	benzo(a)pyrene
Ba	barium
BLM	Bureau of Land Management (see MMS)
CalCOFI	California Cooperative Oceanic Fisheries Investigations
Cd	cadmium
CDFG	California Department of Fish and Game
CDHS	California Department of Health Services
CMW	California Mussel Watch
Co	cobalt
Cr	chromium
CSDLAC	County Sanitation Districts of Los Angeles County
CSDOC	County Sanitation Districts of Orange County
Cu	copper
DDE	1,1-dichloro-2,3-bis(p-chlorophenyl)ethylene
DDT	dichlorodiphenyltrichloroethane
dw	dry weight
EPA	Environmental Protection Agency
FAC	fluorescent aromatic compounds
FDA	Food and Drug Administration
FFPI	fossil fuel pollution index
GC/ECD	gas chromotography/electron capture detection
GC/MS	gas chromotography/mass spectroscopy
Hg	mercury
HMW	high molecular weight
HTP	Hyperion Treatment Plant
JWPCP	Joint Water Pollution Control Plant
kg	kilograms
km	kilometers
LARWQCB	Los Angeles Regional Water Quality Control Board
LA-LB	Los Angeles-Long Beach harbors
LMW	low molecular weight
m	meters
MAHs	monocyclic aromatic hydrocarbons
MBT	monobutyl tin
MBC	Marine Biological Consultants
MBL	Marine Bioassay Laboratories
Mg	magnesium

mg/kg	milligrams per kilogram
MGD	million gallons per day
MLML	Moss Landing Marine Laboratory
MMS	Minerals Management Service
Mn	mangenese
Mo	molybdenum
NAS	National Academy of Science
Ni	nickel
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NOSC	Naval Ocean Systems Center
NPMP	National Pesticide Monitoring Program
NRC	National Research Council
NS&T	National Status and Trends
NSSP	National Shellfish Sanitation Program
OAD	Ocean Assessments Division
OCEMA	Orange County Environmental Management Agency
OCS	Outer Continental Shelf
OES	optical emission spectrometry
PAH	polycyclic aromatic hydrocarbons
Pb	lead
PCB	polychlorinated biphenyls
PNAHs	polynuclear aromatics hydrocarbons (polyaromatics)
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
Pu	Plutonium
SCCWRP	Southern California Coastal Water Research Project
Se	selemium
Sn	tin
Sn IV	inorganic tin
STP	sewage treatment plant
SWRCB	State Water Resource Control Board
t	total
TBT	tribulytin
TOC	total organic carbon
tPAH	total polycyclic aromatic hydrocarbons
tPCB	total polychlorinated biphenyls
U.S. EPA	United States Environmental Protection Agency
U.S. FDA	United States Food and Drug Adminstration
USCD	University of Southern California, Davis
V	vanadium
W	tungsten
WHO	World Health Organization
ww	wet weight
ZID	zone of initial dilution
Zn	zinc
µg/g	micrograms per gram

ZID	zone of initial dilution
Zn	zinc
µg/g	micrograms per gram